UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ENGENHARIA MECÂNICA
E INSTITUTO DE GEOCIÊNCIAS

OSWALDO IVAN KLINGER CATAÑO

OIL RECOVERY IN CARBONATE RESERVOIR ROCKS BY REDUCING TOTAL SALINITY OR NaCl IN INJECTION WATER FOR CORE FLOODING TESTS

EFEITOS PRODUZIDOS PELA REDUÇÃO DA SALINIDADE TOTAL E NACL NA RECUPERAÇÃO DE PETRÓLEO EM CARBONATOS DO PRÉ-SAL BRASILEIRO

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Dissertation presented to the Mechanical Engineering Faculty and Geosciences Institute of the University of Campinas in partial fulfillment of the requirements for the degree of Master in Petroleum Sciences and Engineering in the area of Reservoirs and Management.

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Coorientador: Dr. Eddy Ruidiaz Muñoz

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DISSERTAÇÃO DE MESTRADO ACADÊMICO

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This work is dedicated firstly to God who gave me the opportunity of starting this walk in the right place. Secondly, my family and friends for being there always. Finally, to my grandparents, “mis viejos” here I AM.

“Without commitment you will never start, but more importantly, without consistency you will never finish”. Denzel Washington.

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ABSTRACT

To investigate the effects of reducing total salinity and NaCl in the injection water on carbonate plugs under real reservoir conditions, a set of three coreflooding experiments for each case were performed. The results allowed the identification of the effects of low salinity water injection in oil recovery, and the influence of some rock mineral dissolution or precipitation in the permeability of the porous media. Experiments were performed under reservoir conditions, reservoir core plugs and live oil. The experimental apparatus was designed to mimic a secondary, tertiary and ultimate stage of the oil production. Firstly, the reservoir plugs were cleaned, dried, saturated with formation water and flooded with dead oil to obtain the initial saturation of water. Secondly, the samples were aged for at least two weeks to restore the wettability of the rock. Thirdly, cores were assembled in a hassler core-holder to switch the oil phase, from crude oil to live oil present in the rock, and finally, three brines in each case with different salinities and different concentrations of NaCl were injected in the rock to evaluate its oil recovery in each test. Experiments showed which brine would have the best oil recovery in a secondary stage; however, no additional oil recovery was obtained by the reduction of the total salinity or reduction in NaCl in the injection brine. Values of pressure drop obtained during the test by pressure transducers installed in the apparatus showed a decrease in some cases with the injection of some reduced brine salinity, leading to think that the permeability of the porous media had an increase because of mineral dissolution.

Palavras Chave: Low salinity; NaCl reduction; Total salinity reduction.

RESUMO

Para investigar os efeitos da redução da salinidade total e NaCl na água de injeção em carbonatos sob condições reais de reservatório, um conjunto de três experimentos de dislocamento forçado para cada caso foi realizado. Os resultados permitiram a identificação dos efeitos da injeção de água com baixa salinidade na recuperação de óleo ea influência de alguma dissolução ou precipitação do mineral na permeabilidade do meio poroso. Os experimentos foram realizados sob condições de reservatório, amostras de reservatório e óleo vivo. O aparato experimental foi projetado para imitar um estágio secundário, terciário e final da produção de petróleo. Primeiramente, as amostras foram limpas, secos, saturados com água de formação e inundados com óleo morto para obter a saturação inicial da água. Em segundo lugar, as amostras foram envelhecidas por pelo menos duas semanas para restaurar a molhabilidade da rocha. Em terceiro lugar, os núcleos foram montados em um porta-núcleo hassler para trocar a fase oleosa do petróleo morto para o óleo vivo presente na rocha e, finalmente, três salmouras em cada caso com diferentes salinidades e diferentes concentrações de NaCl foram injetadas na rocha. avaliar sua recuperação de óleo em cada teste. Experimentos mostraram qual salmoura teria a melhor recuperação de óleo em um estágio secundário; no entanto, nenhuma recuperação adicional de óleo foi obtida pela redução da salinidade total ou redução de NaCl na salmoura de injeção. Valores de queda de pressão obtidos durante o teste por transdutores de pressão instalados no aparelho mostraram uma diminuição em alguns casos com a injeção de salinidade de salmoura reduzida, levando a pensar que a permeabilidade dos meios porosos teve um aumento devido à dissolução mineral.

Palavras chaves: Baixa salinidade; Redução da salinidade total; Redução do NaCl.

FIGURE LIST

CONTENTS

1. INTRODUCCION AND MOTIVATION

Carbonate reservoirs are valued to hold approximately 60% of the world's oil reserves. (BP, 2016) estimated those reserves in 1707 billion barrels in 2016. Carbonate's formation usually presents common characteristics, such as high heterogeneity, low permeability, and oil/neutral wettability which only 30 to 40% of the oil in place can be recovered by traditional waterflooding (CHANDRASEKHAR; SHARMA; MOHANTY, 2016).

Traditional oil recovery methods engage primary production by reservoir pressure depletion followed by secondary production methods. The most common secondary method is water flooding which leaves behind a sizeable residual oil saturation of 60-70%. The low efficiency of water flooding in carbonate reservoirs is because they are characteristically non-water-wet and highly heterogeneous in the pore-perm system; these properties are not favourable for water flooding method leaving un-swept zones. These properties cannot be improved yet; however, a method that could alter the wetting properties to a more water-wet state only by altering the ionic composition of the injection water can give a significant improvement in oil recovery from many formations.

A large number of enhanced oil recovery (EOR) methods have been investigated in carbonates formations for more than 50 years; surfactant-polymer injection is one of them. However, extreme reservoir conditions, as well as high cost of implementation, limit the use of surfactant-polymer flooding; high temperatures and salinities negatively affect polymers; besides, low permeability causes mechanical deterioration of the method. The enormous potential that shows the injection of calibrating water is due to the facility to apply, and it is a relatively cheap method to be implemented as a secondary or tertiary recovery method compared to chemical methods for example. Brine composition and salinity have been extensively studied for many years; however, research in carbonates has not been studied as much as in sandstones, the reason of this is that initially it was believed that this method could not be applied in carbonates because of their lack of clay contains, (ALSHAIKH; MAHADEVAN, 2016).

The research work started by University of Stavanger (AUSTAD et al., 2005) has shown that sulphate ions play an important role in oil recovery from carbonate reservoirs. Because of the adsorption, these ions alter the wettability and consequently increase water-wetness. It proposed that injection brine with high sulphate, coupled with high temperatures, would give higher recovery by spontaneous imbibition. Another study (FATHI; AUSTAD; STRAND, 2011) pointed out that not only sulphates and divalent such as Ca^{2+} and Mg^{2+} are essential, but also the amount of non-active ions (Na^+ and Cl^-) affect the wettability alteration in carbonates. Therefore, selective water ionic composition with a specific monovalent to divalent ion content is required for improving the wetting properties on carbonates formations, which constitutes complex water chemistry compared to sandstones, and thereby requires better tuning and flexibility in the water chemistry of injection water, (AYIRALA; YOUSEF; ARAMCO, 2014).

The general schedule for the set of experiments was a group of Pre-Salt reservoir cores, live oil and brines at reservoir conditions. Those elements aim the potential enhance oil recovery of the brines in the proposed sequences of salinity. In this work, two strategies of EOR based on low salinity waterflooding will study the effect on oil recovery in both secondary and tertiary mode using variations of the concentration of monovalent ions (Na^+ and Cl^-) and total salinity of the injection water at real reservoir conditions.

1.1. Objectives

The scope of this study is to evaluate the potential seawater injection into carbonate rocks. Moreover, identify the effects of depleting the concentration of Na^+ and Cl^- and reduction of total salinity, which can produce additional oil linked to wettability alteration. The study was prepared to obtain a better understanding of the low salinity effect on carbonate rock and the mechanism behind wettability alteration. Besides, compare the oil recovery obtained at reservoir conditions.

- Analyse the impact on oil recovery by reducing the total salinity in carbonates at reservoir condition.
- Study the effect of depleting sodium chlorine in the oil recovery of carbonate reservoirs.
- Develop an experimental set-up able to work under reservoir conditions.

2. BIBLIOGRAPHIC REVIEW

This chapter presents the main concepts needed to understand the technique of advanced oil recovery by injecting water with reduced salinity. Concepts such as carbonate reservoirs and their petrophysical characteristic will be addressed as well as the principal factors and ions that play an essential role in the technique. It will present experimental evidence on the injection of low salinity water and reduction of total salinity, in addition, the mechanisms behind the increase in oil recovery suggested by researchers.

2.1. Carbonates

Carbonates for definition are anionic complexes of (CO3)2- and divalent metallic cations such as Ca, Mg, Fe, Mn, Zn, Ba, Sr, and Cu (WAYNE M. AHR, 2008). Carbonates occur naturally as sediments and reefs in modern tropical and temperature oceans, as ancient rocks, and as economically valuable mineral deposits. The common carbonates are grouped into families, they are known by the crystal systems in which they form. The most common carbonate minerals are in the hexagonal system, notably calcite (CaCO3) and dolomite (CaMg(CO3)2). Aragonite is typical in the modern oceans, but it is rare in the ancient rock record; therefore, it is safe to say that carbonate reservoirs and aquifers are composed of calcite and dolomite. Together, those rocks make up about 90% of all naturally occurring carbonates.

Carbonates have attributes that distinguish them from siliciclastic and that require different methods of study. Firstly, carbonates from within the basin of deposition by a biological, chemical, and detrital process. They do not owe their mineralogical composition to weathered, parent rocks and their textures do not result from the transport down streams and rivers. Carbonates are primarily made up of skeletal remains and other biological constituents. Secondly, carbonates depend significantly on biological activity that is a big difference between carbonates and siliciclastics. They are composed mainly of biogenic constituents, grain size and shape changes as organisms ate them, burrowed, and boring organisms extensively modify the stratification of carbonate rock bodies. Finally, carbonates are susceptible to rapid and extensive diagenetic change.

Minerals that composed the carbonate rock are susceptible to rapid dissolution, cementation, recrystallization, and replacement at ambient conditions in a variety of diagenetic environments, (LUCIA, 1999; WAYNE M. AHR, 2008).

Carbonate reservoirs store more than 50% of the known petroleum reserves (STRAND; HØGNESEN; AUSTAD, 2006), which can split into three rock types: limestones, chalks, and dolomite. On average, the oil recovery in these sorts of rocks is low reaching sometimes only the 30% of the original oil in place (OOIP) due to the characteristic of carbonate rocks. The principal challenges of recovering oil from those rocks are low permeability, natural fractures, heterogeneities in rock properties, and low water wetness.

AUSTAD, 2013; AUSTAD et al., 2005 pointed out that at relevant reservoir conditions the carbonate surface is positively charged. The carboxylic material in crude oil, as determined by the Acid Number (mgKOH/g), is the most critical wetting for carbonate/rock/brine, (CBR)-system. The bond between the negatively charged carboxylic group, -COOH-, and the positively charged sites on the carbonate surface is stable, and the large molecules will cover the carbonate surface. Therefore, the low water wetness in carbonate rocks that difficult the oil recovery in those kinds of reservoirs.

2.2. Wettability

Wettability can be defined as the solid surface's preference for one fluid over another immiscible fluid in contact with a solid surface; one of the phases is usually attracted to the surface more strongly than the other phase. This phase is identified as the wetting phase while the other phase is the non-wetting, (WILLHITE, 1986).

The force balance between two immiscible fluids (water and oil) at the contact line between them determines wettability of a surface. Figure 1(A) illustrates the forces that are present at the contact line are σ_{os}, the IFT between the solid and the oil phase; σ_{ws}, the IFT between the solid and the water phase; and σ_{ow}, the IFT between the oil and water phase. In this case, the contact angle is measured through the water phase to σ_{ow}. Figure 1(B) shows water-wet and oil-wet systems.

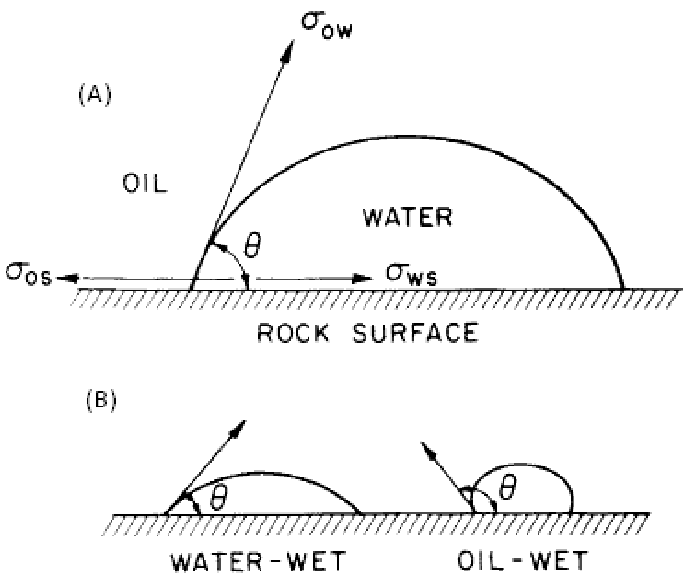


Figure 1.Wettability in a water/oil/rock system. (A) Interfacial forces in a system with two immiscible fluids. (B) Description of a water-wet and oil-wet system, (WILLHITE, 1986)

The principal measure for wettability is the contact angle θ in a smooth, homogenous surface, at equilibrium, the sum of the forces acting along the contact line must be zero, (WILLHITE, 1986).

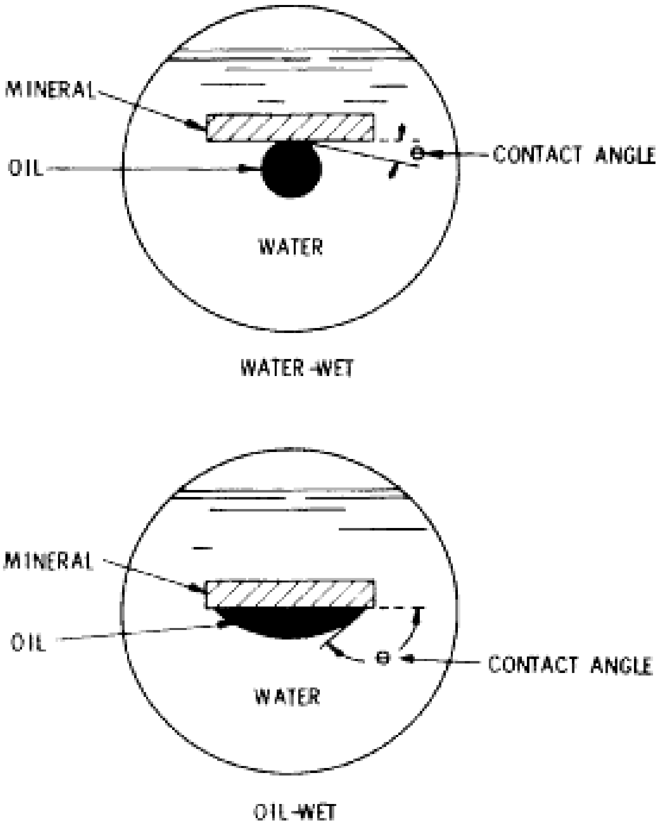


Figure 2 - Contact angles measured through the aqueous phase, (WILLHITE, 1986)

In petroleum reservoirs, wettability state affects the distribution, orientation and fluid flow in porous media. The classification of the wetting properties relates when interpreting contact angles in practice. Figure 2 illustrates examples of water-wet and oil-wet systems. Water wet systems are those with contact angles between 0° to 75°. Oil-wet systems, which have contact angles from 105° to 180°. Systems with contact angles between 75° to 105° are referred to as having intermediate wettability, (JOSÉ ROSA, ADALBERTO. DE SOUZA CARVALHO, RENATO. DANIEL XAVIER, 2006; WAYNE M. AHR, 2008).

2.2.1. Wettability by crude oil

Double layer Theory

All minerals have a specific electrical charge, which would vary depending on the purity of the mineral and the fluid surrounding. The pH of the fluid that is surrounding the surface plays an essential role in the surface charge because of depending on that value the surface would have a specific charge. There is a pH value when the surface charge vanishes (point of zero charges), this value for calcite ($CaCO_3$) is 9.5, therefore, for all values of pH below the surface charge would be positive, (SCHECHTER, 1992). Depending on that charge, the surface would attract organic compounds or ions with the opposite charge. Thus, the chemical interaction with the crude compounds with the electrical charge of the rock could determine the wetness of the rock (THOMAS; CLOUSE; LONGO, 1993). Figure 3 shows a sketch double layer for a negatively charged surface mineral, analogously for a positively charged surface. This theory is used to explain some mechanisms behind wettability alteration in carbonates.

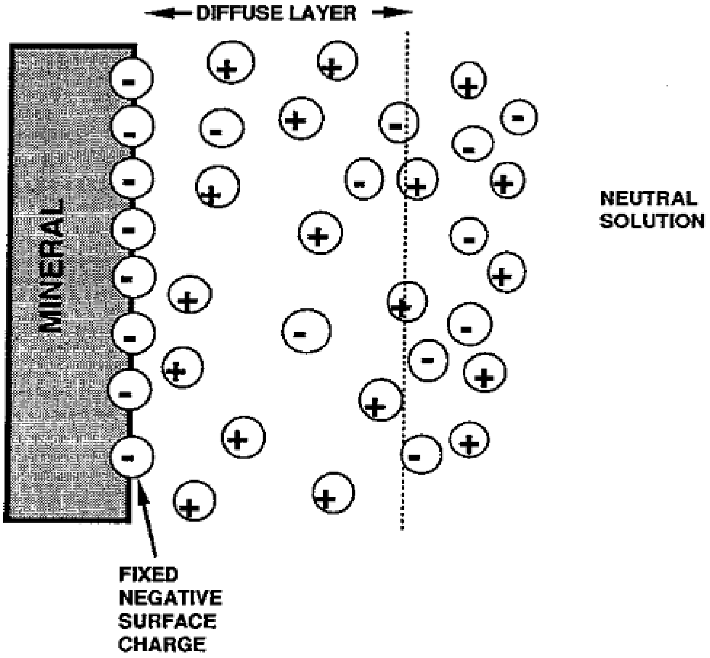


Figure 3 - Sketch showing the distribution of charge near to a mineral surface. Source:(SCHECHTER, 1992)

Crude Oil Wetting

It assumed that in water-wet reservoirs conditions, water had initially been in the reservoir when the migration of oil occurred. As oil accumulated, water was retained by capillary forces in the smallest pore spaces and as films on pore surfaces overlain by oil. Chemical interaction such as adsorption of polar compounds from crude oil plays a critical role in determining the wetting properties of the reservoir-rock surface (MORROW, 1990). That adsorption phenomenon is greater on calcite than quartz because, under comparable conditions, calcite has more positive surface charged dragging closer the carboxylic fraction of oil altering wetting properties, (MORROW, 1990). Wettability alteration has been linked to the adsorption of high-molecular-weight colloidal particles known as asphaltenes suspended in oil crude, (CHANDRASEKHAR; SHARMA; MOHANTY, 2016).

The acid number, AN (mgKOH/g) determines the quantity of carboxylic material will be present in the oil; moreover, it is the important wetting parameter for carbonate systems, (STANDNES; AUSTAD, 2000). Crude oil components which contain the carboxyl group, -COOH, are mostly found in the heavy end fraction of crude oils (Resin, asphaltene fraction, and naphthenic acids). The affinity between the negatively charged carboxylic group (-COO$^-$) and the positively charged sites on carbonate surface is very strong, and large molecules will cover the carbonate surface. Figure 4 shows a clear example of how the acid number affect the imbibition in Chalks cores saturated with oils of different AN.

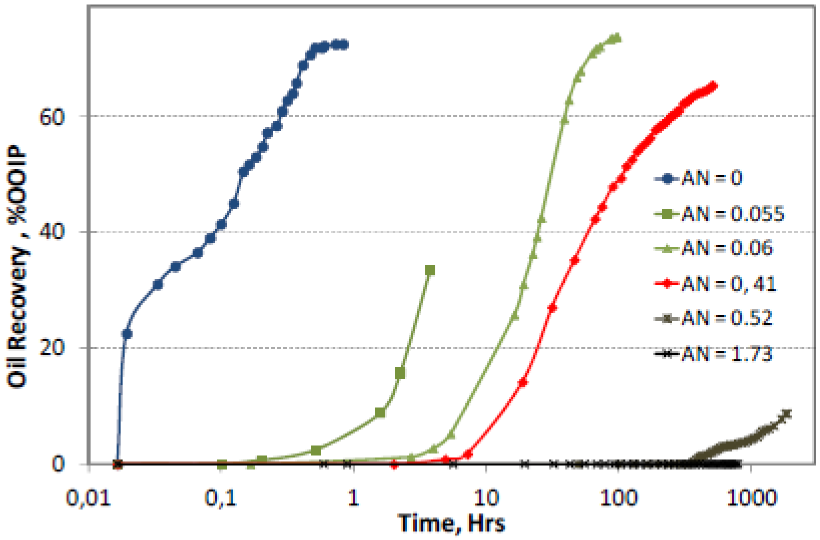


Figure 4 - Spontaneous imbibition into chalk cores saturated with different oils. Source:(STANDNES; AUSTAD, 2000)

ZHANG; AUSTAD, 2005 also shows the importance of the acid number in the wettability on chalks. In this experiment, oils with a different acid number (AN) were used, the imbibing curves show a lower oil recovery with the increase of AN. On the other hand, the imbibing curves that represent the displacement of oil with a lower acid number show a better performance, therefore, a lower acid number higher oil recovery.

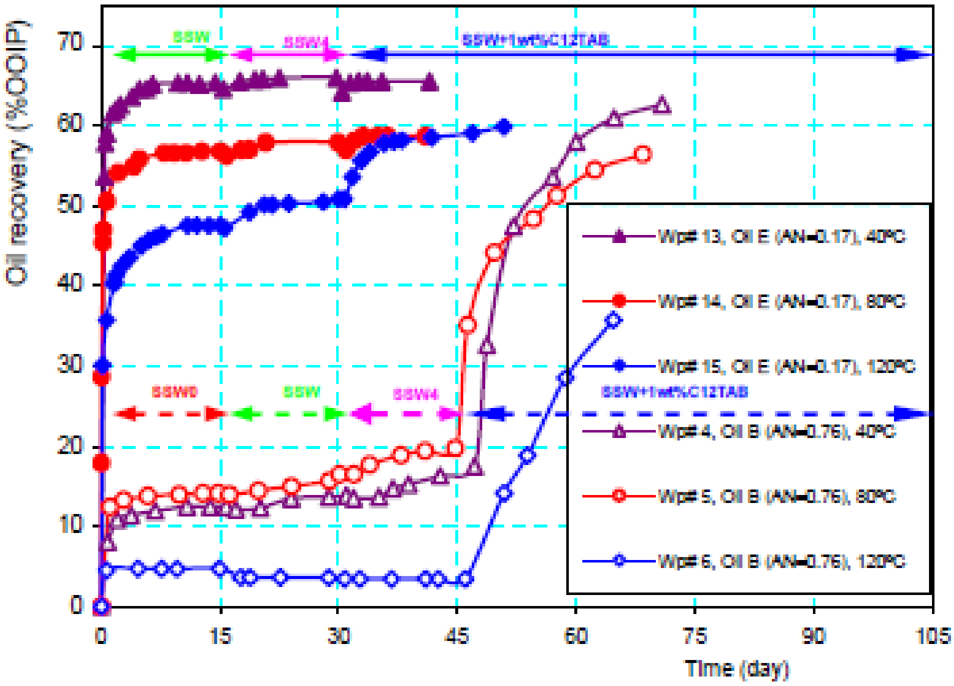


Figure 5 - Typical spontaneous imbibition performance with oils with different acid number. Source: (ZHANG; AUSTAD, 2005)

2.3. Mechanisms for wettability modification by low salinity water in carbonates.

Several studies in the past decade have shown that the composition and the salinity of the injection water in conventional waterflooding can enhance the oil recovery in carbonate rocks (AUSTAD et al., 2005; TANG; MORROW, 1999).

The mechanisms that have gained more acceptation in the community are rock dissolution (HIORTH; CATHLES; MADLAND, 2010; YOUSEF et al., 2010, 2011) and multi-ion exchange (AUSTAD, 2013; AUSTAD et al., 2005; ZHANG; TWEHEYO; AUSTAD, 2007). Despite the various studies behind the oil recovery by the injection of low salinity water, the chemical mechanisms of wettability change are not fully understood.

2.3.1. Dissolution

Dissolution of carbonates has been well documented in geology researches. Injection of brine not in equilibrium with the carbonate can push mineral-brine kinetics towards dissolution, which can lead to wettability alteration as new rock layer, untouched by oil, is exposed.

AUSTAD et al. 2012 found in his experiments that the presence of anhydrite ($CaSO_4$) could improve oil recovery by its dissolution. The sulfate in the porous medium may be present in its solid form ($CaSO_{4(s)}$, mainly), adsorbed onto the carbonate surface ($SO_4^{2-}{}_{(ad)}$) or dissolved in the pore water ($SO_4^{2-}{}_{(aq)}$). The dissolution of anhydrite, $CaSO_{4(s)}$, which is the primary source of $SO_4^{2-}{}_{(aq)}$ would increase oil recovery in a low salinity waterflooding scheme.

In other study, (HIORTH; CATHLES; MADLAND, 2010) developed a thermodynamic model that takes into account the chemical composition of the water, the adsorption of the surface and the dissolution/precipitation of minerals in order to calculate how different properties of the brines can affect the behavior of the electric charge on the rock surface. HIORTH; CATHLES; MADLAND, 2010 concluded that incremental oil recovery is not related to changes in the rock surface charge. Therefore, they proposed the dissolution mechanisms in order to explain their results.

When the temperature is above 60°C the dissolution of calcite will take place, and the enhance imbibition is observed. When anhydrite formation takes places, the aqueous phase loses calcium, and calcium has yielded from the rock for the solution to remain in equilibrium with calcite. The source of Ca^{2+} ions must be calcite dissolution. If the calcite dissolution takes place where the oil is being absorbed, then the oil would be liberated from the rock.

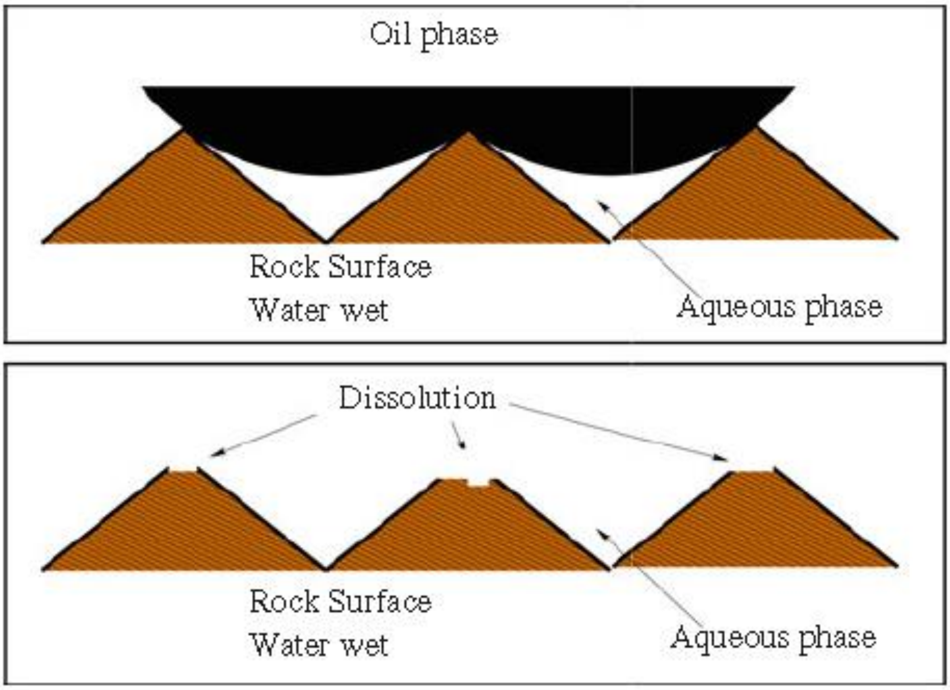


Figure 6 - Dissolution of the chalk surface has taken place where the oil attached. (HIORTH; CATHLES; MADLAND, 2010)

Figure 6 illustrates the dissolution mechanism, the image above shows a simplified model of the porous media before any dissolution. On the other hand, the inferior part of Figure 6 shows that the dissolution of calcite removes oil located after the injection of low salinity water.

YOUSEF et al., 2010 and YOUSEF et al., 2011 performed tests of nuclear magnetic resonance (NMR) in composite carbonate rocks before and after low salinity waterflooding. They observed that the macropores and micropores connection was enhanced. Improving that connectivity can be attributed to microscopic dissolution generated by injecting different salinity slugs of seawater, or salinity gradient initiated because of initial formation water is not easy to replace by subsequent slugs of seawater. Figure 7 shows another indication of dissolution of the rock; it was the constant reduction of pressure rock throughout the tests.

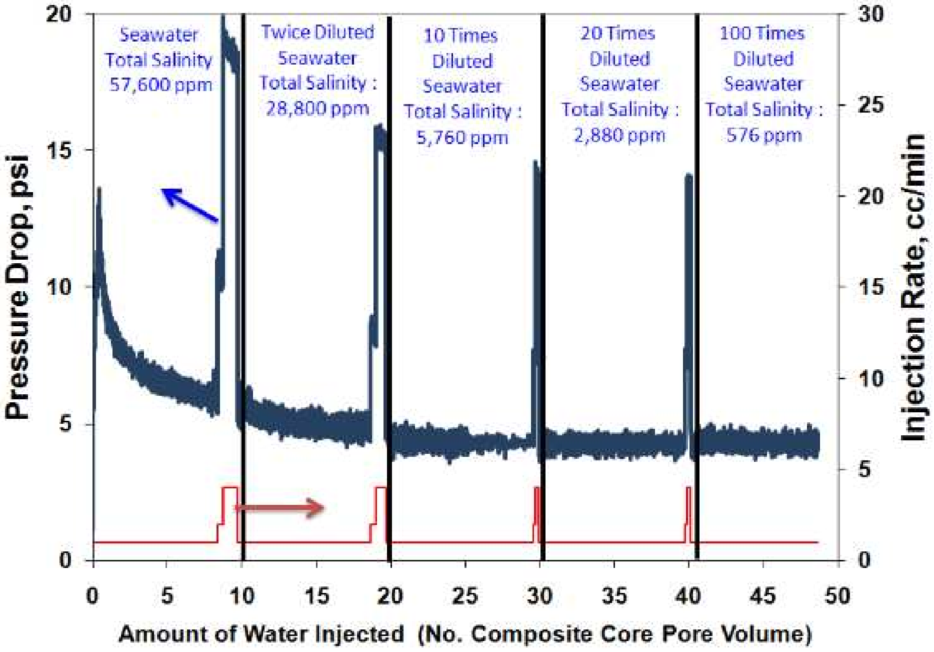


Figure 7 - Pressure drop curve vs pore volumes injected. The dark blue represents the pressure drop and the red curve represents the injection rate profile. Source: (YOUSEF et al., 2010)

2.3.2. Multi-ion exchange

AUSTAD, 2013; AUSTAD et al., 2005 says that initially, the surface rock is positively charged due to a pH<9 and high concentration of Ca^{2+} and possible some Mg^{2+} in the formation water. The concentration of SO_4^{2-} in the formation water is too small to consider relevant. As “Low salinity water” is injected into the carbonate reservoir, SO_4^{2-} will adsorb onto the positively charged surface and lower the positive charge. Due to less electrostatic repulsion, the concentration of Ca^{2+} close to the surface is increased, and Ca^{2+} can bind to the negatively charged carboxylic group and release it from the surface. Both concentrations, SO_4^{2-} and Ca^{2+} at the carbonate surface increases as the temperature is increased.

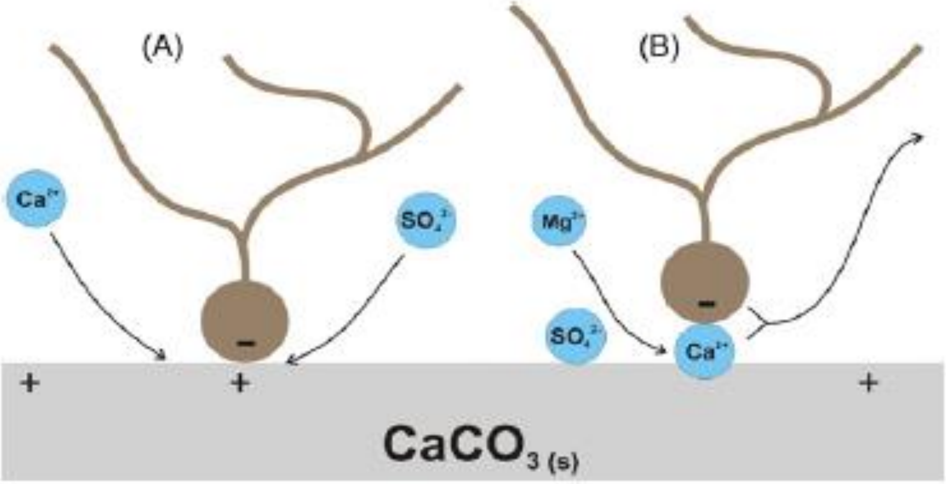


Figure 8 - Schematic model of suggested mechanism for the wettability alteration induced by seawater. (A) Proposed mechanism when Ca^{2+} and SO_4^{2-} are active at lower. (B) Proposed mechanism when both Ca^{+2}, Mg^{2+}, and SO_4^{2-} can interact at higher temperatures. Source:(ZHANG; TWEHEYO; AUSTAD, 2007)

The ion Ca^{2+} have the capacity of interacting with the carboxylic group absorbed on the surface and release it at low and high temperatures, Figure 8 (A). At low temperatures, the Mg^{2+} cations are generally more hydrated and thus less reactive. On the other hand, at high temperatures, the Mg^{2+} ions are more active and able to substitute the Ca^{2+}. Mg^{2+} ions replace both the Ca^{2+} ions and the complexes of calcium and carboxylic acids ([-COOCa +]) formed on the surface, making the surface of the rock less oil-wet and consequently increasing the recovery factor of the reservoir Figure 8 (B), (ZHANG; TWEHEYO; AUSTAD, 2007).

It can be said that the wettability alteration using Mg^{2+} and SO_4^{2-} is only active at high temperatures supports the suggested mechanism. It is unlikely that the small and strongly solvated Mg^{2+} can substitute Ca^{2+} in a Ca^{2+}–carboxylate complex when the temperature is under 90°C as (ZHANG; TWEHEYO; AUSTAD, 2007) suggested in Figure 8(A). Moreover, the Ca^{2+} –carboxylate bond is naturally stronger than the Mg^{2+} – carboxylate bond since Ca^{2+} is a common ion for carbonate rocks, therefore, it is predictable that Mg^{2+} is a weaker potential determining ion towards carbonate surface compare with Ca^{2+}.

In the theory of wettability alteration for carbonates, there are two kinds of ions. The first ones are the active ions, which play an active role in the wettability alteration; the principal ions are sulfate, calcium, and magnesium. On the other hand, there are the non-active ions, which does not have an active role in the ion exchange process but hinder the ability of the active ions,(AUSTAD et al., 2015). Next, it presents some works done in low salinity water injection in order to achieve a better understanding of the role of active ion, non-active ions, and temperature in the technique.

Influence of the calcium ion.

The formation water in carbonate reservoir has a high salinity most of the time as well as a high concentration of calcium ion (Ca^{2+}). Due to the high concentration of Ca^{2+} in the formation water, the rock surface tends to be positively charged. They believe that the ion Ca^{2+} is one of the main reasons why the wettability of carbonate rock is more likely to oil-wet. Therefore, the higher the concentration of Ca^{2+} in the formation water, the greater the oil-wet wettability.

AL-ATTAR et al., 2013 also ran a test varying the concentration of Ca^{2+} in the injection brine from 664 to 1992 ppm in order to see the influence of the ion in the recuperation of oil in the reservoir of Bu Hasa. The Figure 9 illustrates curves of oil recovery versus pore volumes injected; it shows that as the concentration of calcium increase the final oil recovery decrease. Flooding with the original calcium concentration of 332 ppm yielded the highest oil recovery, and by increasing the calcium concentration, the oil recovery decreased.

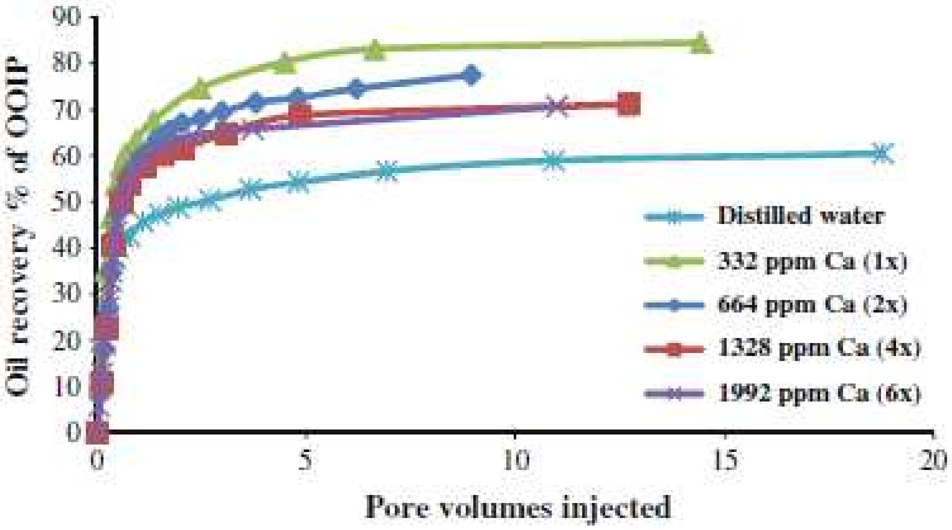


Figure 9 - Oil recovery versus pore volumes injected brine at different Ca2+ concentrations. Source: (AL-ATTAR et al., 2013)

This experiment gives a clear example that high concentrations of calcium affect oil recovery in carbonates negatively, even though calcium is one of the active ions in the ion exchange theory, (AUSTAD, 2013).

Influence of the magnesium ion

ZHANG; TWEHEYO; AUSTAD, 2007 highlighted the importance of Mg^{2+} as a wettability modifier in the presence of SO_4^{2-}. The temperature appeared to be of great importance, and the relative efficiency of Ca^{2+} and Mg^{2+} as wettability modifiers will probably depend on the actual temperature.

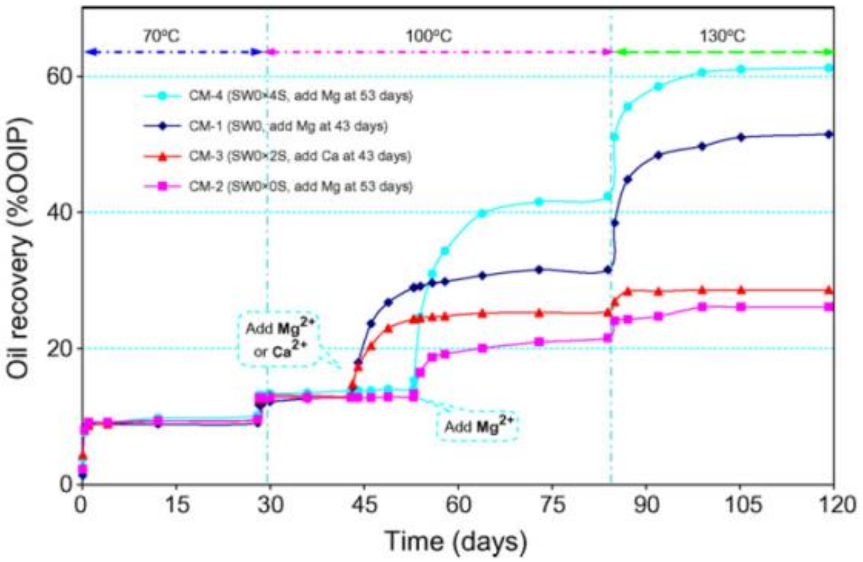


Figure 10 - Result of a spontaneous imbibition test. Modified seawater without Ca^{2+} and/or Mg^{2+} was initially used as imbibing fluids, and later on Ca^{2+} or Mg^{2+} was added with a concentration of seawater concentration. Source: (ZHANG; TWEHEYO; AUSTAD, 2007)

Figure 10 shows the result of the first set of a test by (ZHANG; TWEHEYO; AUSTAD, 2007). As it can be seen, when Mg^{2+} was added in the presence of SO_4^{2-} the recuperation of oil is affected positively (aquamarine line). In the next set of tests, the concentration of sulphate in the imbibing fluid kept constant and similar to seawater, while the concentration of Mg^{2+} was spiked.

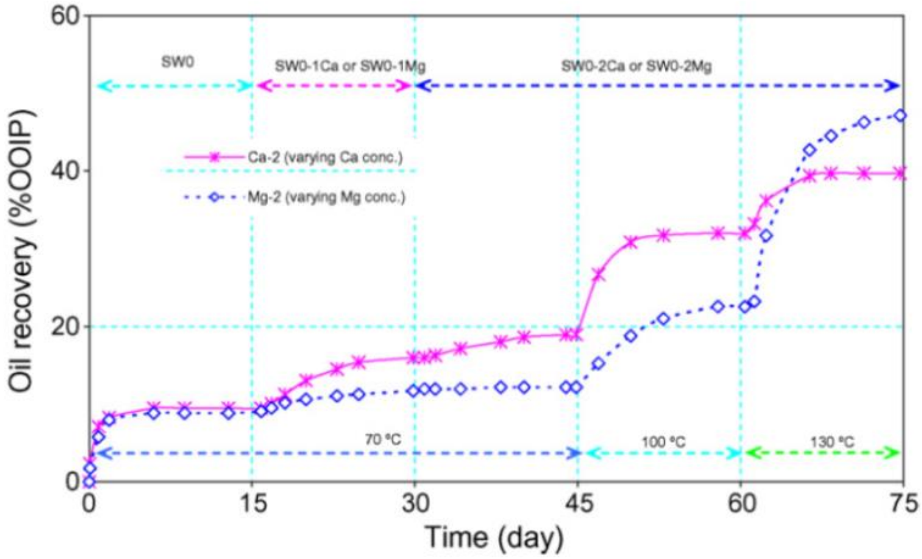


Figure 11 - Result of a spontaneous imbibition when equal amount of Ca^{2+} or Mg^{2+} was added gradually into imbibing fluids with SO_4^{2-}. Source: (ZHANG; TWEHEYO; AUSTAD, 2007)

Some improvements regarding oil recovery were observed when adding Ca^{2+} to the imbibing fluid; however, less than 20% of the oil was recovered after 45 days. Only a minimal amount of oil was recovered after adding Mg^{2+} to the imbibing fluid. At 130°C, the core imbibed with Mg^{2+} in the brine produce more oil than the core imbibed with Ca^{2+} in the brine. If the imbibing fluid contains Mg^{2+}, which is the case for seawater, precipitation of $CaSO_4$ can be avoided, and Mg^{2+} can even act as an additional wettability modifier at high temperatures. Finally, they conclude that it is experimentally verified that Mg^{2+} is also a strong potential determining ion towards the chalk surface, which has the potential to increase the positive charge density of chalk. Moreover, at high temperatures, Mg^{2+} present in seawater can substitute Ca^{2+} from the chalk surface, and the degree of substitution increase with the temperature.

Influence of sulphate ion

Some researchers have seen the vital role that the sulphate ion plays in the wettability alteration. (AUSTAD et al., 2005) and his team at the Stavanger University worked on cores from Tor formation to understand the principle behind the successful injection of seawater into the Ekofisk chalk field in the North Sea. In addition, the outstanding performance of the seawater injection into the Ekofisk formation is an indication of a specific rock-water interaction, which improves the spontaneous displacement of oil.

They found that the concentration of sulphate ion in the seawater has a positive influence on the chalk surface charge. As a result, the injected seawater readily imbibes spontaneously into the reservoir matrix and improves the oil recovery. In order to have a better understanding of the sulphate ion in the alteration of wettability towards more water-wet, some additional tests were carried out. Samples from Stevens Klint were taken and saturated with Mixed-brine (Formation water / Seawater = 1/3) and then flooded with oil until residual saturation (AN=1,7 mgKOH/g). The cores were aged for four weeks at 90°C. The test was conducted at 70°C. They varied the concentration of sulphate ion keeping the salinity constant by adjusting the NaCl-concentration as the Figure 12 shows. This work demonstrates the critical role of the sulphate ion in the oil recovery in those rocks, a higher concentration of the sulphate ion represents a higher oil recovery. They propose that the waterfront should be as high as possible in sulphate concentration, in order to avoid a low concentration in the waterfront because of the adsorption onto the chalk surface.

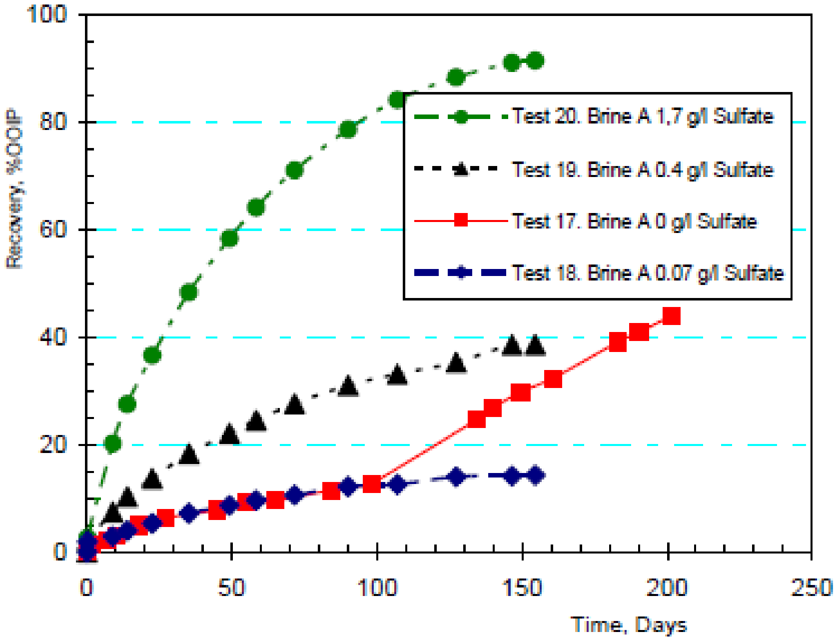


Figure 12 - Oil recovery % versus time, effect of sulphate ion on spontaneous imbibition. Source: (AUSTAD et al., 2005)

(AL-ATTAR et al., 2013) also saw the effect of the sulphate ion, although, they took different core material to work on. The samples were taken from the Bu Hasa field in Abu Dhabi. In order to investigate the effect of the sulphate ion, they varied the concentration of sulphate from 11.7 to 70.2 ppm. As a result, the increase in the concentration of sulphate in the seawater injected trending to intermediate-wetness levels, which end up improving oil recovery. However, an optimum sulphate concentration is the responsible for shifting the system's wettability. The Figure 13 summarizes up the results that the obtained varying the sulphate ion.

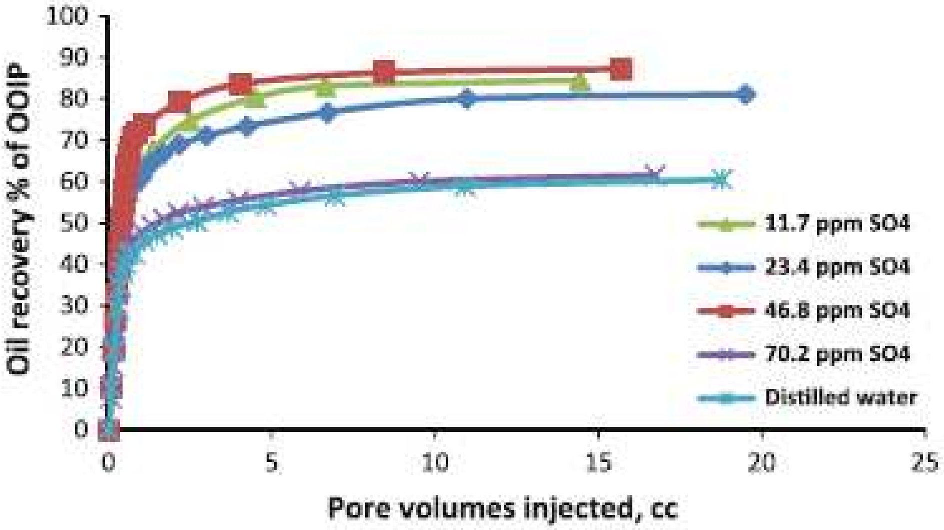


Figure 13 - Oil recovery versus pore volumes injected of each brine with different concentration of sulphate ion. Source: (AL-ATTAR et al., 2013)

(STRAND; HØGNESEN; AUSTAD, 2006) also attempt to investigate the mechanism for spontaneous imbibition of seawater into preferential oil-wet chalk. Concluding that, the potential determining ions towards chalk, Ca^{2+}, and SO_4^{2-} are essential in wettability alteration process. The adsorption of SO_4^{2-} onto chalk surface facilitates the desorption of negatively charged carboxylic materials by changing the surface charge of the chalk which lowers the positive charge density of the carbonate rock surface and facilitates some desorption of the carboxylic material from the surface, (TWEHEYO; ZHANG; AUSTAD, 2006).

Influence of the temperature

According to (TWEHEYO; ZHANG; AUSTAD, 2006), the temperature can play an essential role in the wettability alteration when the ion calcium is present, because when they kept the sulphate ion constant and increased the concentration of calcium the imbibition process end up in better performance at increasing temperature.

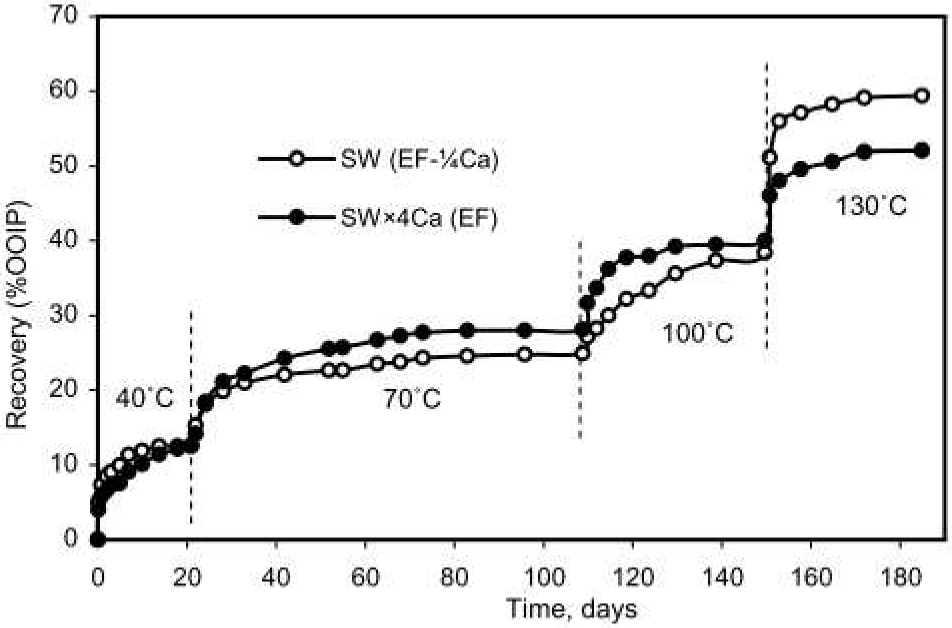


Figure 14 - Imbibition at 40, 70, 100, 130°C using different calcium, sulphate ratio concentration in the initial and imbibing brines. Source: (TWEHEYO; ZHANG; AUSTAD, 2006)

Figure 14 shows how the temperature can affect the oil production behaviour. As it can be seen, in this case, 40°C, increasing the concentration of calcium in the imbibing fluid by four times does not show any significant change on oil recovery. (TWEHEYO; ZHANG; AUSTAD, 2006) explains this phenomenon by the affinity of sulphate adsorption and related chemical reactions are rather slow at this temperature. However, the two curves were separated at higher imbibing temperatures of 70 and 100°C, a higher calcium concentration in initial brine and imbibing fluid resulted in an additional recovery. Nevertheless, the situation reversed at 130°C; the decrease in recovery could be due to precipitation of $CaSO_{4\,(s)}$.

Another work carried out by (ZHANG; AUSTAD, 2006), shows the importance of temperature in the efficiency of wettability alteration process in the presence of sulphate when the temperature increased. In this work, they did spontaneous imbibition test in outcrop chalk from Stevens Klint varying the concentration of sulphate, both below and above the seawater concentration and temperature. In addition, they used two oil with different acid number (oil A=2.07mgKOH/g, and oil B=0.55mgHOH/g).

Figure 15 illustrates an oil recovery (%OOIP) versus time, for different imbibing fluids, the experiment runs during 30 days, and the increment in oil recovery with the concentration of sulphate in the imbibing fluid was relevant. The concentration of sulphate varied from zero up to four times the sulphate present in the seawater. With a concentration of sulphate spiked four times related to seawater, the oil recovery achieved approximately 55% while without sulphate present; reached only 14%. Therefore, oil recovery increased massively as the concentration of sulphate is spiked.

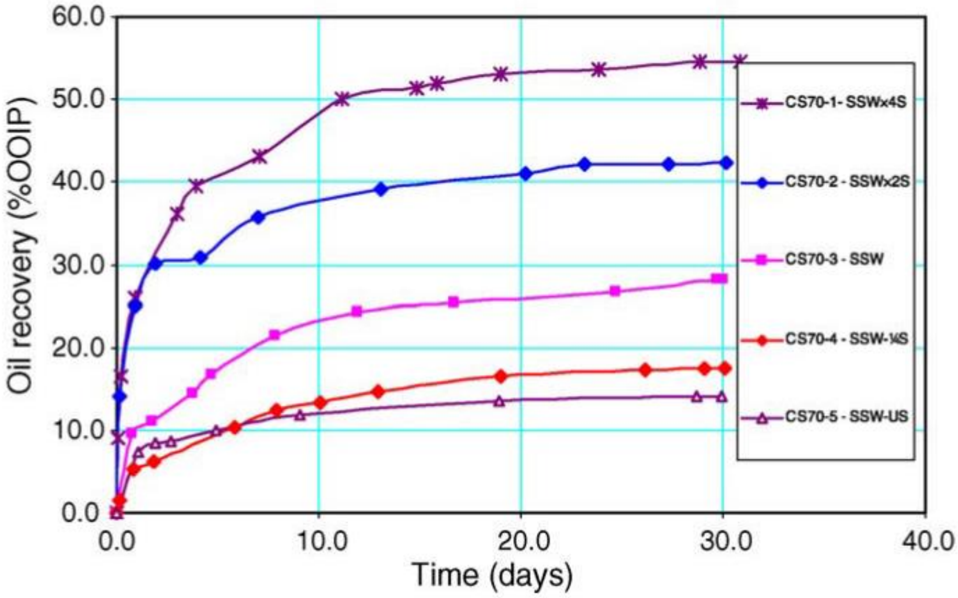


Figure 15 - Imbibition test at 70°C using Oil B (AN=0.55 mgKOH/g) varying the concentration of SO_4^{2-} in the imbibing fluid. Source: (ZHANG; AUSTAD, 2006)

They performed a test with Oil A (AN=2.07 mgKOH/g) at different temperatures of 100°C and 130°C. As we can see in Figure 16, the oil recovery is slightly inferior compared with the test performed at 70°C due to the higher acid number of the Oil A, and it was explained in previous sections the oil recovery is affected negatively by the increase of the acid number. It is important to notice that the only imbibing fluid, which reached a plateau before 30 days was the seawater without sulphate and with an oil recovery close to only 10% of the OOIP.

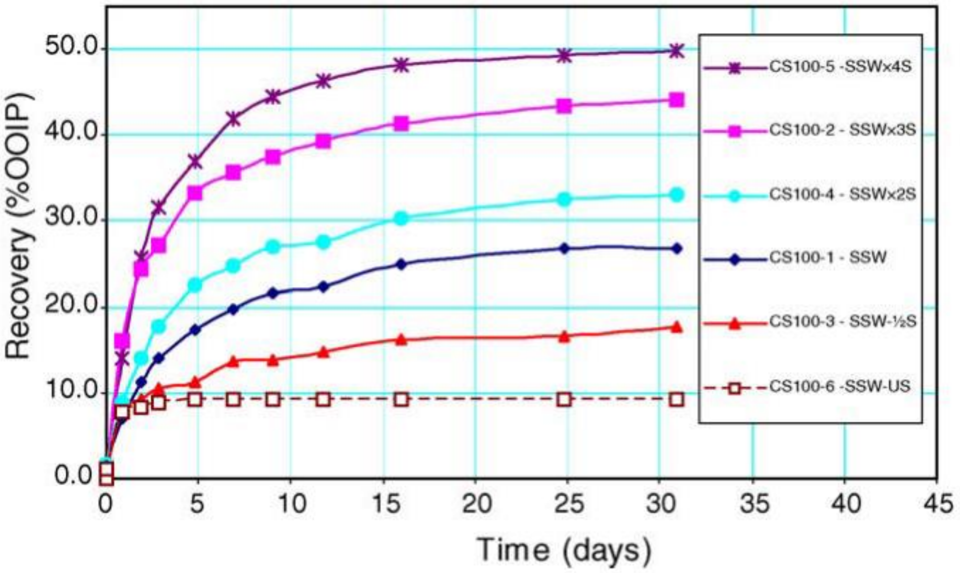


Figure 16 - Imbibition test at 100°C using Oil A (AN=2.07 mgKOH/g) varying the concentration of SO_4^{2-} in the imbibing fluid. Source: (ZHANG; AUSTAD, 2006)

On the other hand, in the experiments performed at 130°C, the production of oil was much faster reaching the plateau before ten days. Besides, the oil recovery was higher at this temperature with 65% of the oil, recovered by the water four and two times spiked with sulphate, Figure 17.

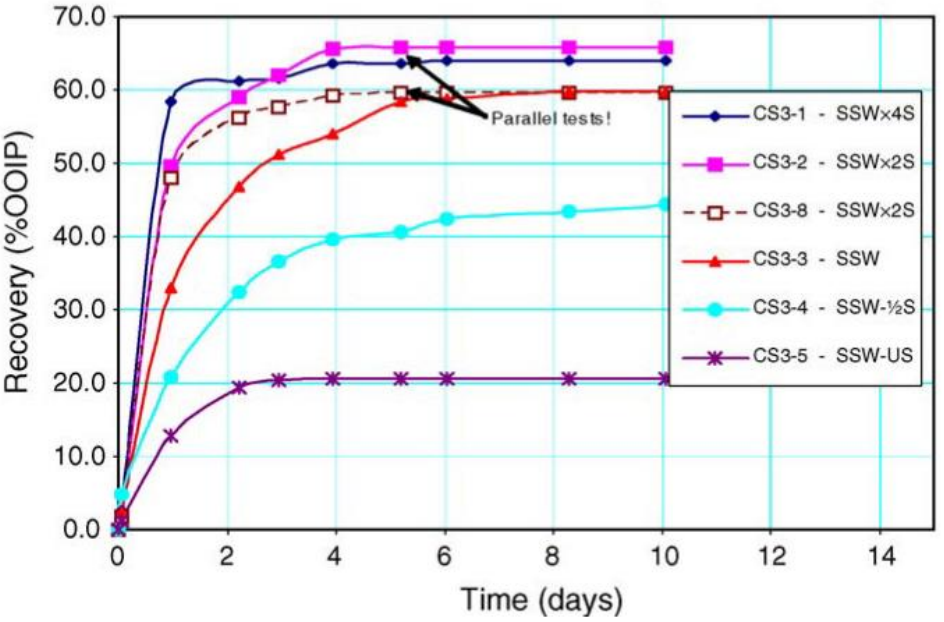


Figure 17 - Imbibition test at 130°C using Oil A (AN=2.07 mgKOH/g) varying the concentration of SO_4^{2-} in the imbibing fluid. Source: (ZHANG; AUSTAD, 2006)

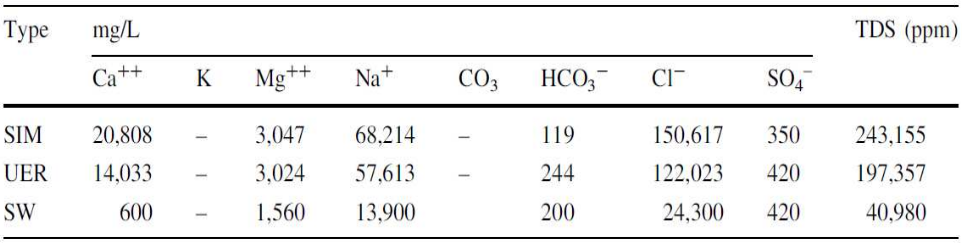
Based on these results, they conclude that the temperature can affect the efficiency of the wettability alteration process in the presence of sulphate positively. Therefore, high temperatures have a favourable effect on the wettability alteration.

Reduction of the total salinity

AL-ATTAR et al., 2013 worked with samples from Bu Hasa field in Abu Dhabi. In this work, they used three different injection waters UER, SIM (formation waters), seawater, as well as distilled water; Table 1 illustrates the compositions of those brines. In the first set of tests, they wanted to observe, which conditions affect the oil recovery by reducing the salinity of the first brine (UER). To evaluate the effect of the salinity, they ran tests varying the salinity of the formation waters. Firstly, they diluted UER to one-half of its original salinity, then to 5,000 ppm and finally to 1,000 ppm; Figure 18 shows the results. The lowest oil recovery percentage observed when using distilled water showing that it not only reducing the salinity of the water, it has to have an ionic composition able to interact with the rock and propitiate the wettability alteration.

On the other hand, the 5,000 ppm performed the best percentage of oil recovery. Therefore, they consider that salinity as the optimum salinity. Furthermore, it is essential to address that not only the total salinity but also having in count the concentration balance between active and non-active ions.

Table 1 - Analysis of the different types of water. Source: AL-ATTAR et al., 2013



Type	mg/L								TDS (ppm)
	Ca^{++}	K	Mg^{++}	Na^{+}	CO_3	HCO_3^{-}	Cl^{-}	SO_4^{-}	
SIM	20,808	–	3,047	68,214	–	119	150,617	350	243,155
UER	14,033	–	3,024	57,613	–	244	122,023	420	197,357
SW	600	–	1,560	13,900		200	24,300	420	40,980

Source: (AL-ATTAR et al., 2013)

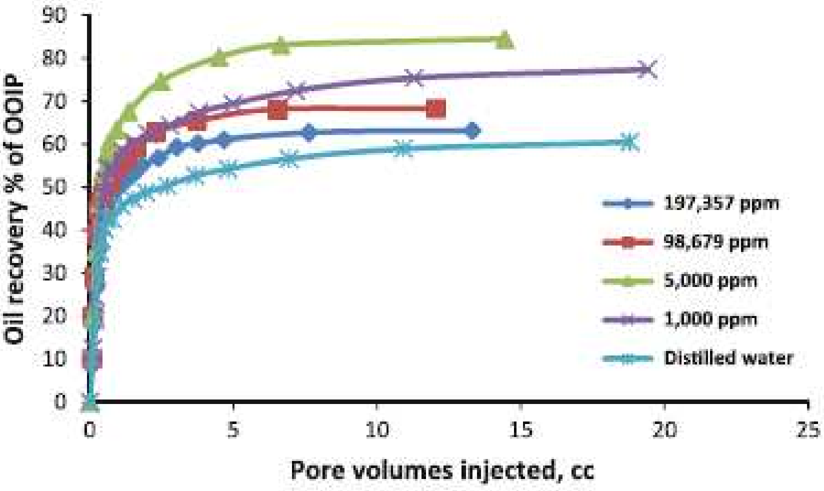


Figure 18 - Oil recovery % versus pore volumes injected of UER water.
Source: (AL-ATTAR et al., 2013)

Secondly, the same set of tests for the SIM water (formation water). As a conclusion, they found that the highest oil recovery achieved with the 1,000 ppm diluted brine, which indicates that the brine salinity with which the porous medium was flooded initially may be related to the salinity at which the technique will have higher efficiency. Moreover, the lowest recovery was with the original SIM water (Figure 19), pointing out that SIM brine has a higher salinity that UER.

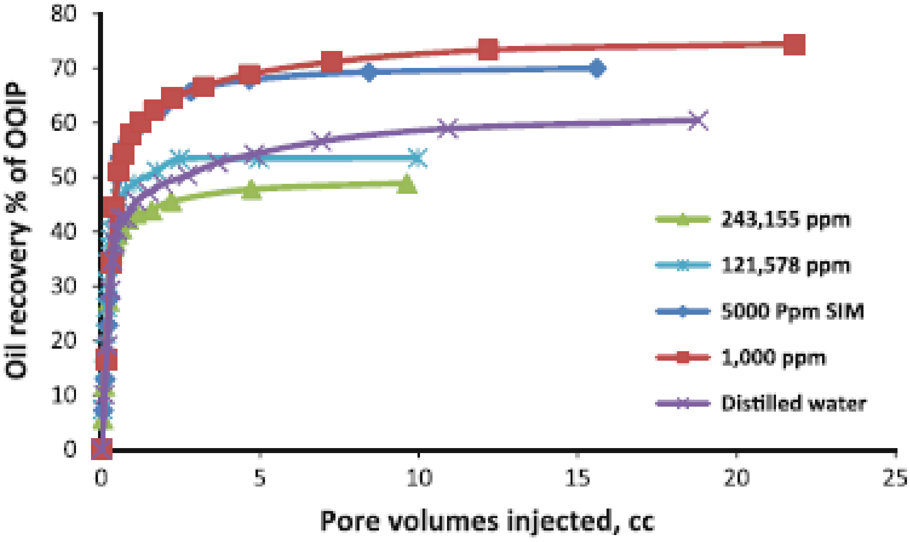


Figure 19 - Oil recovery % versus pore volumes injected of SIM water.
Source: (AL-ATTAR et al., 2013)

Finally, they tested seawater and its dilutions, the only change was that in this test they did not have a half diluted water, the results are shown in Figure 20, a comparable performance and recovering in average 61%, however, the dilutions forms of seawater with salinities of 5000 and 1000 ppm reached the maximum oil recovery in less time. Therefore, they conclude that there is not a significant increase in oil recovery by dilution of seawater but diluted forms have a better performance in oil recovery versus porous volumes injected.

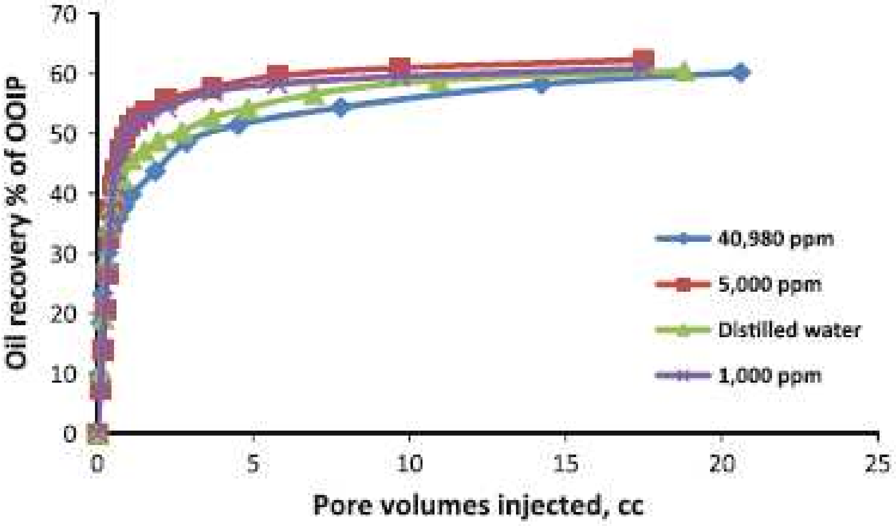


Figure 20 - Oil recovery % versus pore volumes injected of SIM water.
Source: (AL-ATTAR et al., 2013)

YOUSEF; AL-SALEHSALAH; AL-JAWFI, 2011 present a work with laboratory core-flooding studies at reservoir conditions, conducted using composite rock samples from a carbonate reservoir, to investigate the impact of salinity and ionic composition on oil recovery. In addition, they report a broad range of laboratory studies addressing oil recovery mechanism. In order to mobilize the residual oil, a significant reduction in capillary forces is required. IFT measurements between oil, and water, as well as rock wettability measurements (contact angle), are typically used to measure these interactions. ALSHAIKH; MAHADEVAN, 2014 also investigated the variation in IFT with the change in the composition of the brine.

Figure 21 shows different IFT measurements of reservoir live oil with field connate water, regular seawater, and then different diluted versions of seawater. The general trend is that as the salinity of the injection water decrease, and the IFT decrease, (YOUSEF; AL-SALEHSALAH; AL-JAWFI, 2011).

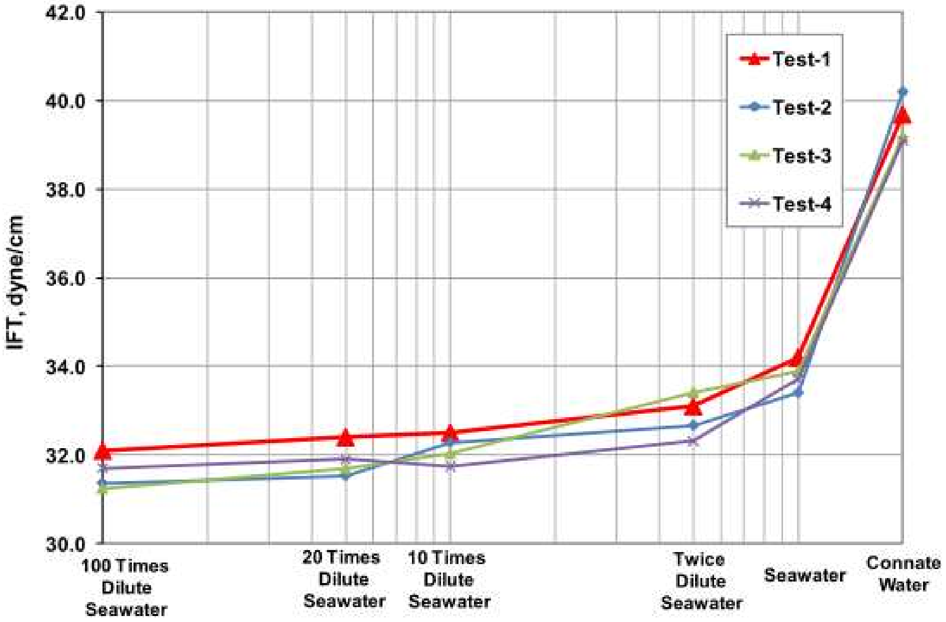


Figure 21 - IFT measurements of reservoir live oil with connate water, injection seawater, and different diluted versions of seawater. Measurements were conducted at reservoir conditions. Source: (YOUSEF; AL-SALEHSALAH; AL-JAWFI, 2011)

Figure 22 shows real images for wettability measurements using connate water, seawater, and different salinity slugs of seawater. As we can see, the contact angle of the connate water is ~ 90°, which indicate intermediate wettability. Regular seawater did not affect the contact angle. They observed a reduction of the contact angle with diluted seawater; contact angle goes from 90° to 69°. However, the most significant changes in contact angles where with twice diluted seawater (from 90° to 80°), and ten times diluted (from 80° to 69°). Almost no alteration with 100 times diluted water, (YOUSEF; AL-SALEHSALAH; AL-JAWFI, 2011).

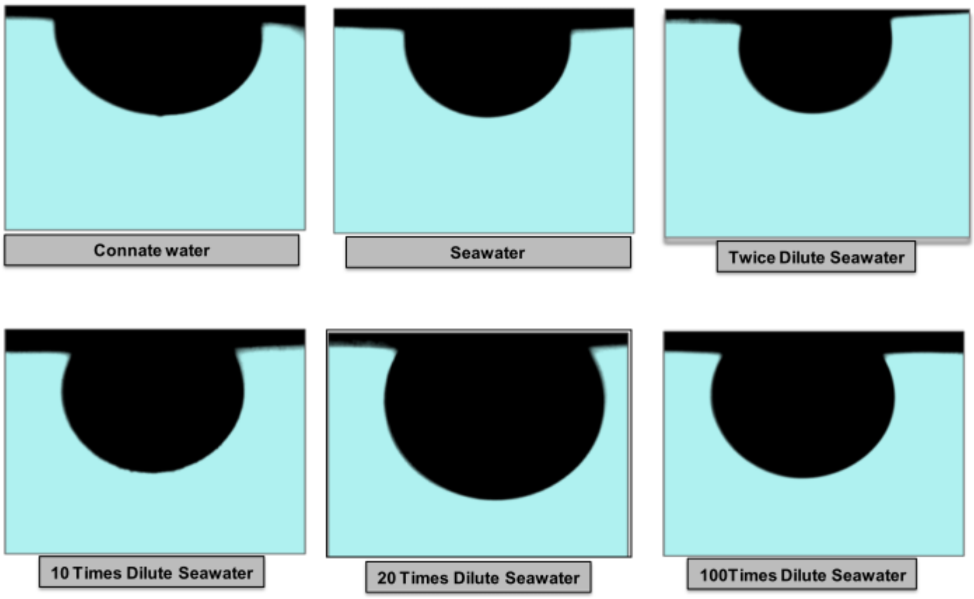


Figure 22 - Contact angle measurements of carbonate rock samples with reservoir live oil and connate water, injection seawater, and different dilution versions of seawater. Measurements conducted at reservoir conditions. Source: (YOUSEF; AL-SALEHSALAH; AL-JAWFI, 2011)

In the core-flood stage, five different salinity slugs of seawater were injected, starting with seawater and ending with 100 times diluted. Figure 23 shows the cumulative oil recovery witch each slug. As we can see, there is an increase in oil recovery until the injection of 10 times diluted, from there; there is not an additional oil recovery.

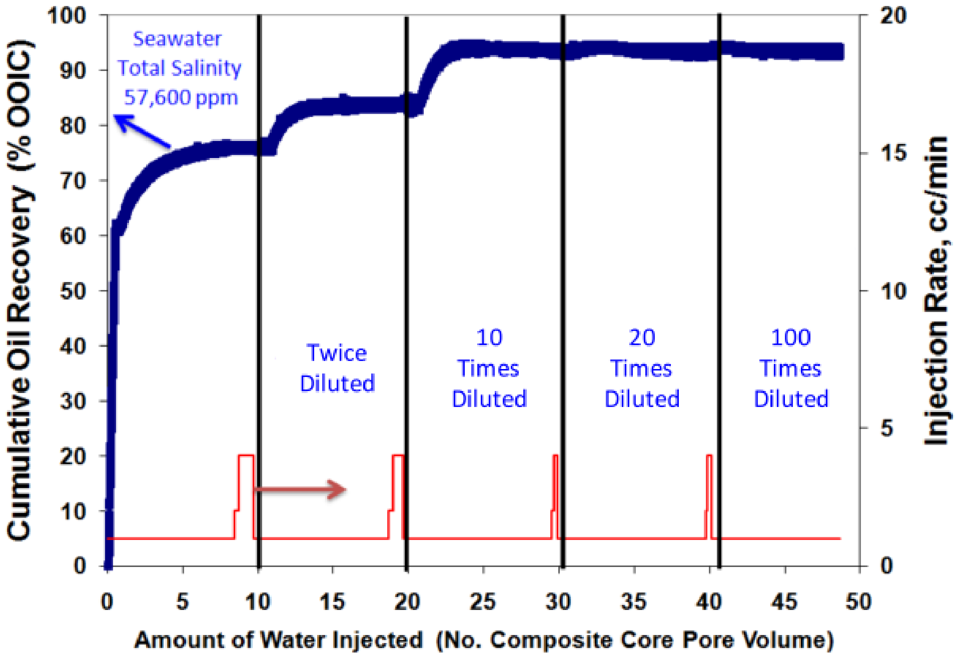


Figure 23 - Oil recovery curve. The blue curve represents the amount of oil produced in terms of original oil in place through all injected salinity slugs of seawater. Source: (YOUSEF; AL-SALEHSALAH; AL-JAWFI, 2011)

AUSTAD et al., 2012 found that the mineralogy of the reservoir rock could play an important role. If the reservoir rock has anhydrite, formation water or seawater diluted can be used as a fluid in the technic. They ran forced displacement tests at 110°C with limestone cores which has a small quantity of anhydrite and Stevens Klint cores without anhydrite. In these tests, they injected in the two kinds of cores first, formation water (208.940 ppm) and then formation water 100 times diluted. In the limestone, it was observed 5% additional oil recovery after the injection of the diluted water Figure 24.

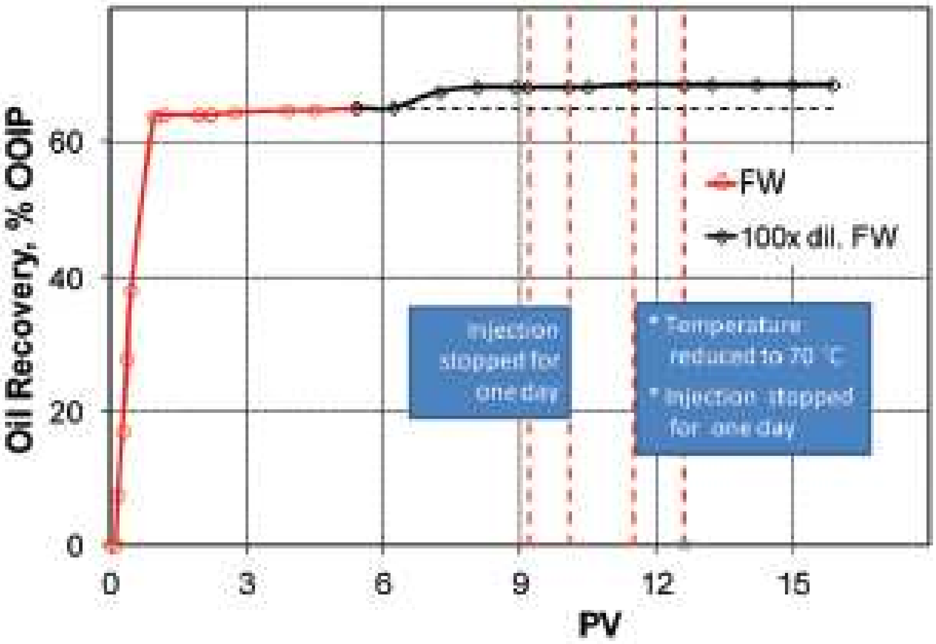


Figure 24 - Oil recovery % versus pore volumes injected, first formation water and then 100 times formation water diluted in Limestone. Source: (AUSTAD et al., 2012)

Even though the formation water has calcium and magnesium ions, it did not have sulphate. The effluent shows a small concentration of sulphate ion, indicating dissolution of $CaSO_{4\,(S)}$ present in the rock Figure 25.

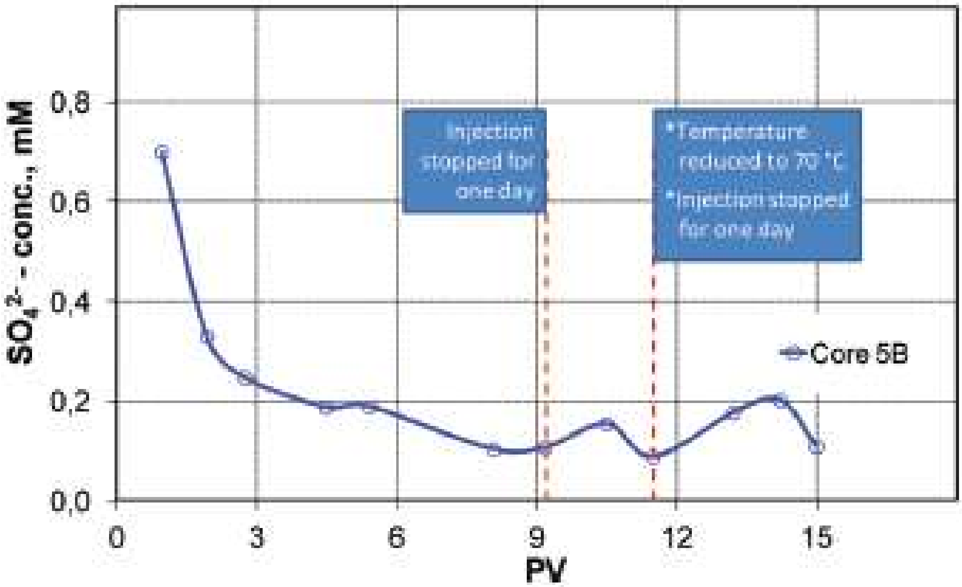


Figure 25 - Concentration of SO_4^{2-} in the effluent versus injected pore volumes. Source: (AUSTAD et al., 2012)

The results that they found in the chalks (without anhydrite) were that the injection of the diluted water did not add any additional oil, Figure 26.

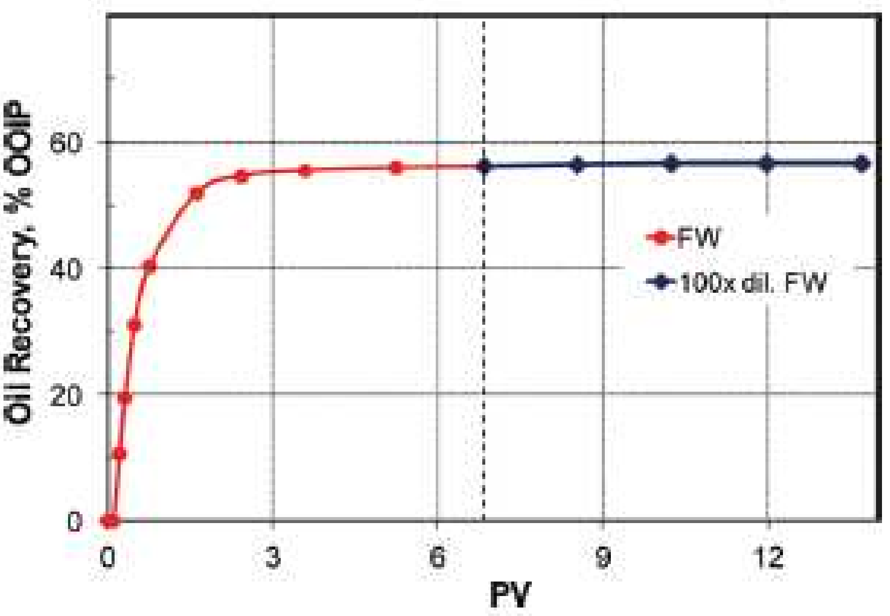


Figure 26 - Oil recovery % versus pore volumes injected, first formation water and then 100 times formation water diluted in Chalk. Source: (AUSTAD et al., 2012)

The researchers conclude that if the reservoir rock has anhydrite in its mineralogical composition, the use of diluted seawater or formation water could be used.

YOUSEF, A. A., AL-SALEH, S., & AL-JAWFI, 2012 show how the IFT changes when the ionic strength decrease, therefore, wettability alteration is induced on the rock. In order to prove how the IFT change with the decrease in ionic strength (YOUSEF, A. A., AL-SALEH, S., & AL-JAWFI, 2012) carried out measurements of the IFT after the injection of seawater and its diluted versions (twice diluted, 10 times diluted, 20 times diluted, and 100 times diluted). The general trend is that when the ionic strength decreases, the rock wettability shifts towards the water-wet state as it seen in Figure 27.

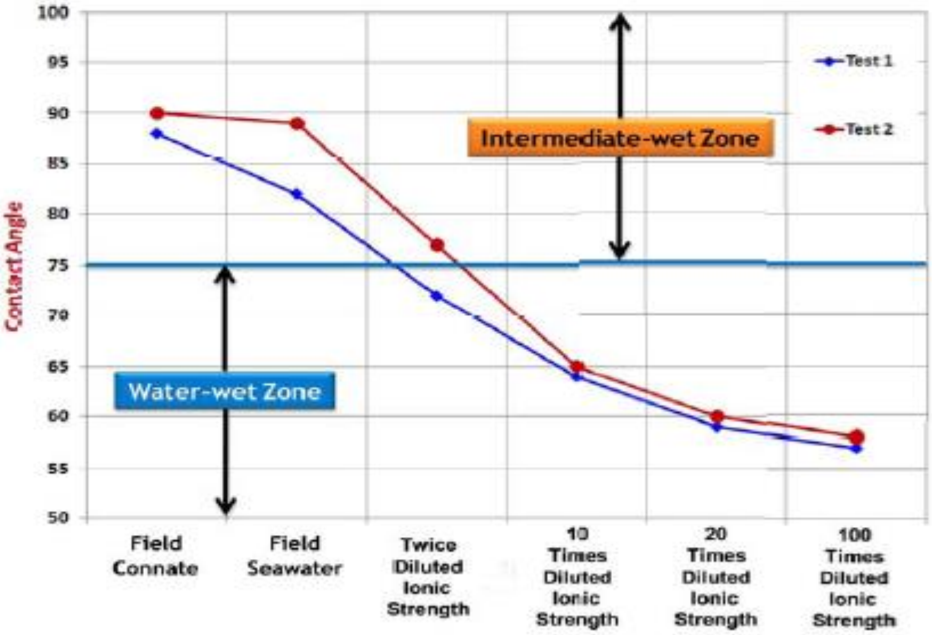


Figure 27 - Contact angles measurements of carbonate rock samples with reservoir live oil and connate water, field water, and different ionic strength of field seawater. Source: (YOUSEF, A. A., AL-SALEH, S., & AL-JAWFI, 2012)

They also performed another test where the brine just contained common ions (Na^+, Cl^-) in order to investigate the role of multivalent ions in the wettability alteration. The result is displayed in Figure 28, showing the experiments carried out for twice-diluted water; exhibit the test presenting wettability alteration toward the water-wet state. However, more dilution did not illustrate a significant alteration in the rock wettability.

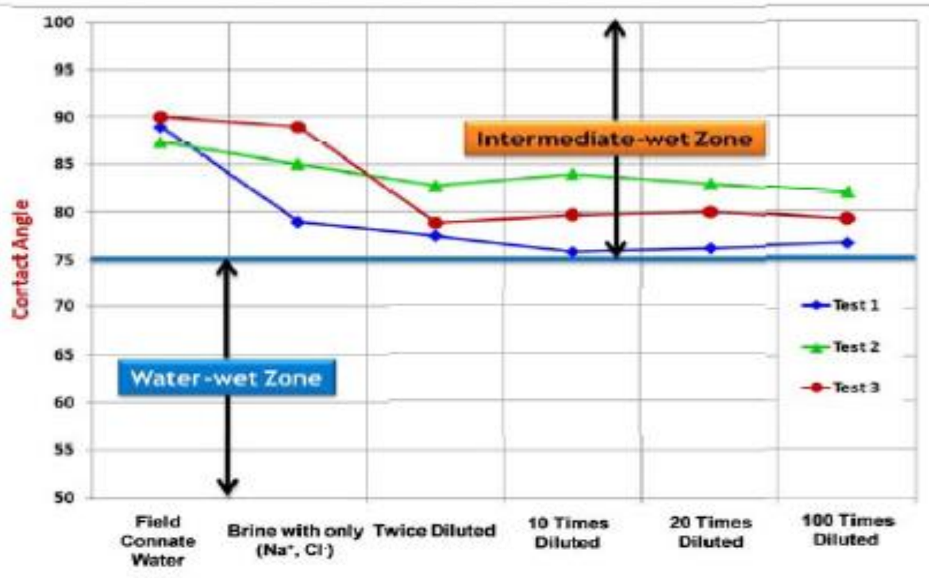


Figure 28 - Contact angles measurements of carbonate rock samples with reservoir live oil and connate water, and set of brines containing only (Na^+, Cl^-), (YOUSEF, A. A., AL-SALEH, S., & AL-JAWFI, 2012)

ZHANG; SARMA, 2012 highlighted the importance of the temperature on the recovery of oil in carbonate rock. However, they do not present results compared with each other. On the one hand, they flooded with seawater and its diluted forms (1/2, 1/10, 1/40 diluted seawater). On the other hand, they flooded with formation water as well as its diluted forms (1/4, and 1/100 diluted formation water). The results show the effect of reducing the total salinity of the injection brine can improve the final recovery.

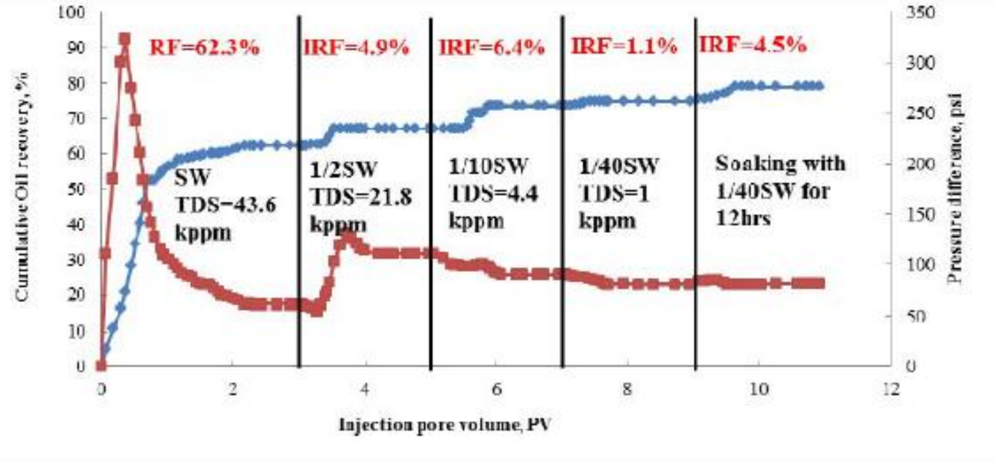


Figure 29 - Cumulative oil recovery and pressure differential curves by injecting Seawater at 70 °C. (ZHANG; SARMA, 2012)

As it can be seen in Figure 29, an increase in the produced oil at each change of water salinity, (ZHANG; SARMA, 2012). However, the recovery by the 1/40 diluted seawater was just 1.1% of OOIP. In addition, the differential pressure was also affected by the change of water salinity, and they do not have a concrete explanation.

Figure 30 shows results of the core-flooding test by injecting formation water and its diluted forms. It can be seen an increment in the oil recovery by reducing the salinity of the formation water.

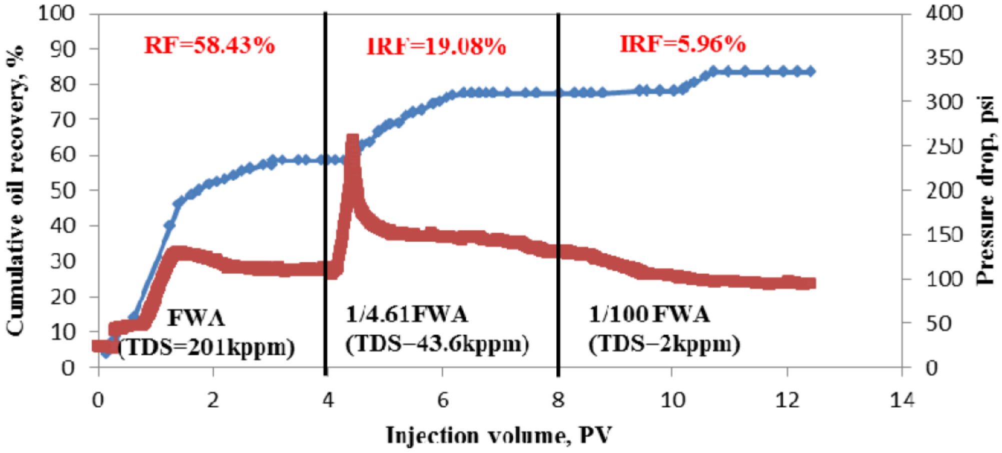


Figure 30 - Cumulative oil recovery and pressure differential by formation water at 120°C. (ZHANG; SARMA, 2012)

At State University of Campinas (UNICAMP), the research group of recuperation by miscible methods (LMMR) have been working on understanding the effects of injecting low salinity water into carbonate rocks. The last work reported by them is the work done by (ANDRADE, 2017). This work used a extreme conditions of temperature (124°C), an injection pressure of 5000 psi, and dolomite outcrops as a rock model to test the evaluate of reducing the total salinity of the injection brine in oil recovery of carbonate rocks.

To find if there is an additional oil recovery when reduced the total salinity (ANDRADE, 2017) performed core-flooding tests varying the injection brine, based on seawater. Therefore, in each experiment, they flooded the rock with three different brines; the sequence of each test is shown in Figure 31.

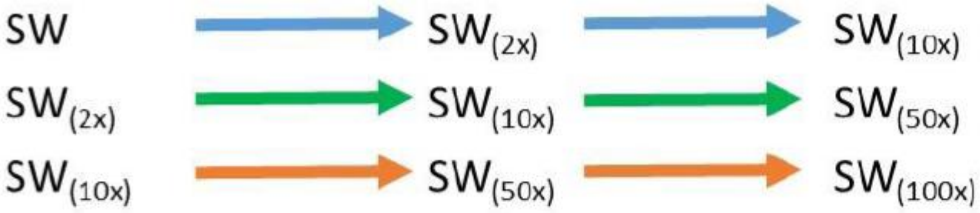


Figure 31 – Sequence of the tests performed. Source: (ANDRADE, 2017)

The experiments performed reducing the total salinity showed strong evidence that it could improve oil recovery in dolomite samples. Seawater obtained 21.08% of the original oil in place (OOIP) recovered, then, with the injection of seawater two times diluted (SW(x2)) 1.65% of OOIP recovered, and not only that, with seawater ten times diluted (SW(x10)) obtained one of the best additional oil recovered results with a 3.63%. Figure 32 illustrates the results obtained by (ANDRADE, 2017).

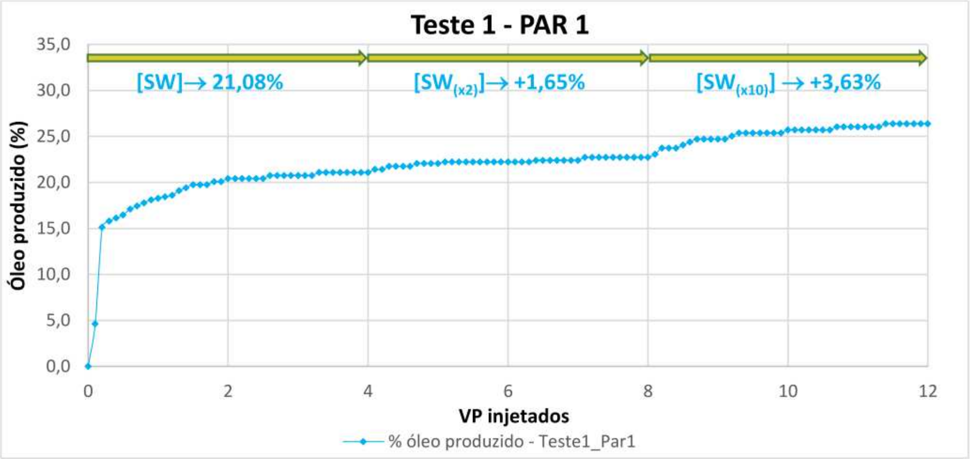


Figure 32 - Oil recovery versus porous volume injected, test one. Source: (ANDRADE, 2017)

After the experiments, they conclude that the reduction of total salinity in the injection brine could improve the oil recovery as it can be seen in Figure 33. However, the total oil recovery in this sort of rocks keeps being low even though there is an additional oil recovery.

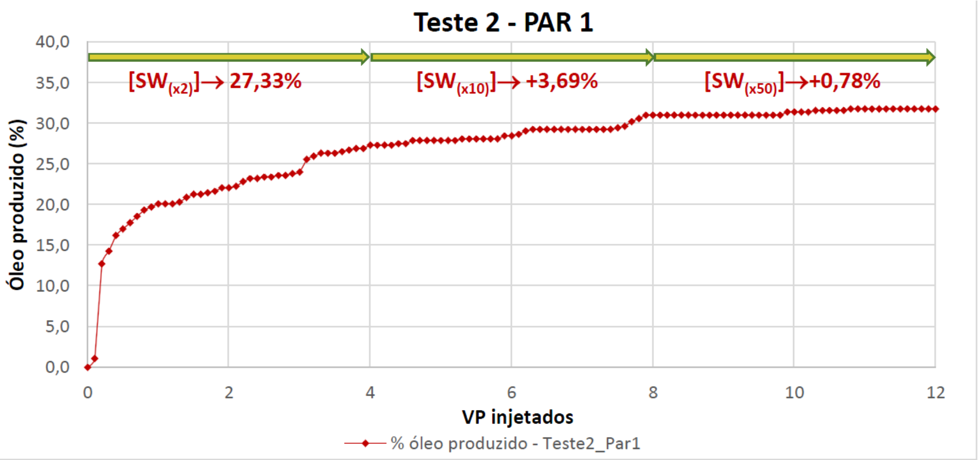


Figure 33 – Oil recovery versus porous volume injected, test two. Source: (ANDRADE, 2017)

The best results that (ANDRADE, 2017) found were when they injected seawater ten times diluted in a secondary stage with an oil recovery of 32% of the original oil in place (OOIP) recovered.

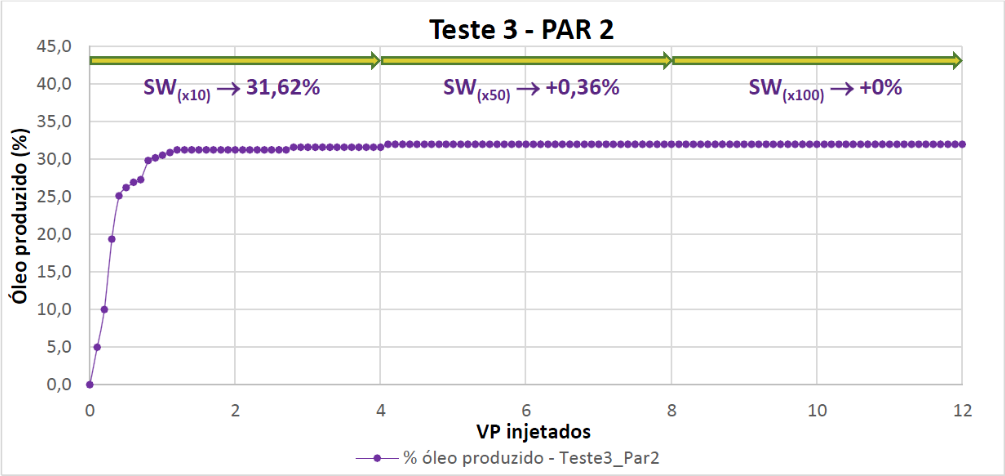


Figure 34 – Oil recovery versus porous volume injected, test three. Source: (ANDRADE, 2017)

It would have been good if they had obtained a differential pressure drop in order to have indications about the mechanism that is acting in the process of wettability alteration. However, the work is very conclusive when it says that diluting seawater could improve the oil recovery in this kind of rocks.

Alteration of NaCl concentration

(FATHI; AUSTAD; STRAND, 2010, 2011, 2012) took the double layer model to explain the mechanism regardless of the rock surface when it depletes the NaCl concentration in the imbibing fluid. They said that the surface would cover by potential determining ions as well as non-potential, as it can be seen in Figure 35.

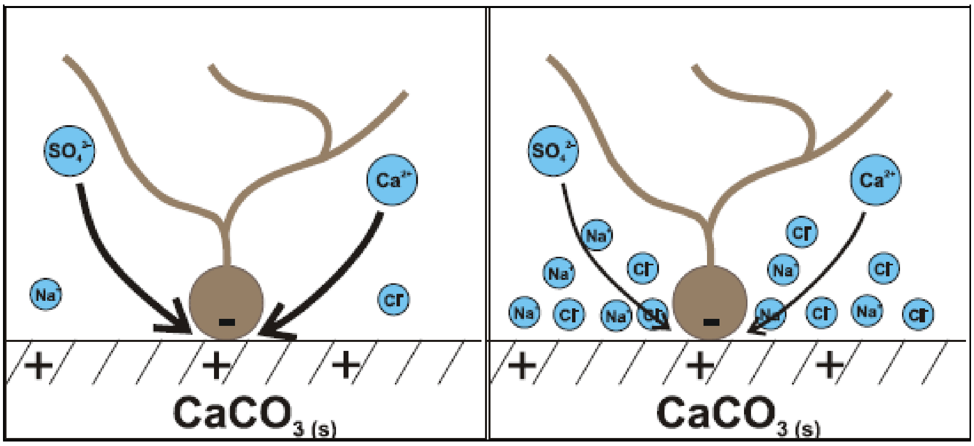


Figure 35 - Diagram of the effect of NaCl. Source: (FATHI; AUSTAD; STRAND, 2012)

The double layer works as a surface cover to the contact with the potential determining ions (SO_4^{2-}, Ca^{2+} e Mg^{2+}), this behaviour is unfavourable to the technic. (FATHI; AUSTAD; STRAND, 2012) worked to increase the understanding of how the concentration of NaCl and dilution of the seawater affect the oil recovery throughs spontaneous imbibition process. In order to accomplish it, in the first experiment it worked at 100°C and three different imbibition fluids, Seawater (SW), Seawater depleted in NaCl (SW0NaCl), and seawater spiked four times the relative concentration of NaCl from seawater (SW4NaCl). Figure 36 shows the result of this test.

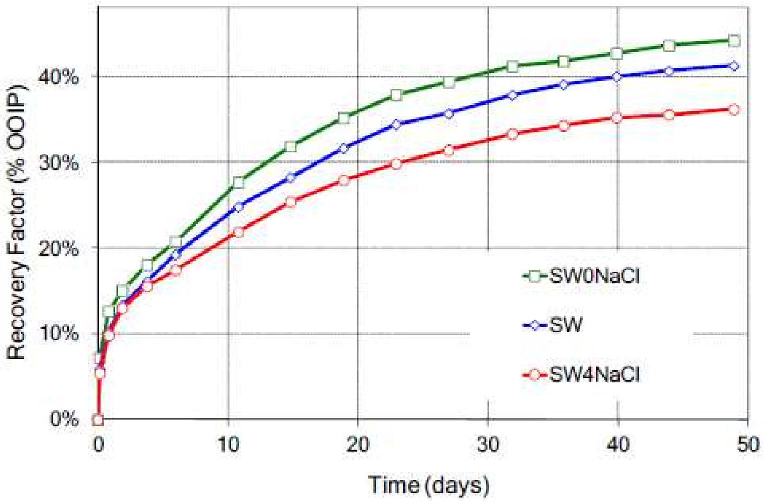


Figure 36 - Spontaneous imbibition into oil saturated oil chalk cores using different imbibition fluids: SW, SW0NaCl, and SW4NaCl. Source: (FATHI; AUSTAD; STRAND, 2012)

As it can be seen, the reduction in NaCl improves is liked with the incremental oil recovery; proving that high concentrations of NaCl can affect the oil recovery in carbonates negatively. Moreover, additional tests where includes aiming the effect on diluted seawater (dSW). Figure 37 displays that seawater without NaCl has the best performance, while the diluted waters did not. The reason for the low recovery they attributed to the decrease in concentration of the active ions, which alter the wetting properties.

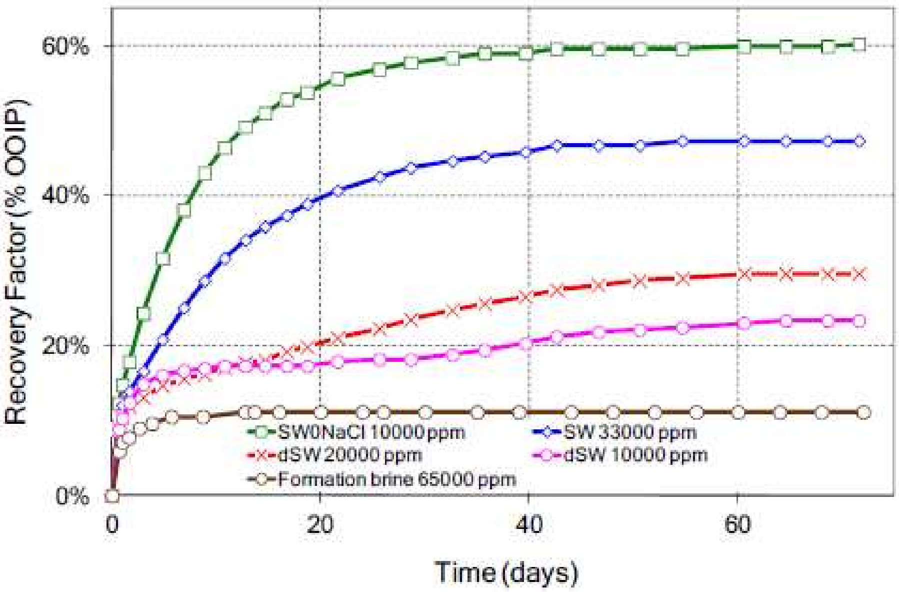


Figure 37 - Spontaneous imbibition into oil saturated chalk cores at 110 °C using seawater (SW), and modified seawater: SW0NaCl, dSW10000, dSW20000, and formation brine. Source: (FATHI; AUSTAD; STRAND, 2012).

Summing up, removing NaCl from the composition improves the oil recovery factor because the active ions have the room the act as a wettability changer. However, diluting seawater to obtain lower salinities brines has a negative impact because when they reduce the total salinity, they are also reducing the concentration of active ions, therefore, the capacity of the water to alter the permeability. Figure 18 shows that by doing that, the recovery factor decreases significantly.

According to (ANDRADE, 2017), NaCl depletion can improve oil recovery in dolomite rocks. To prove that, it performed tests under the same conditions as previously explained to test the effect of sodium chloride reduction in the injection brine on oil recovery of carbonate rocks.

Evaluating the potential of reducing NaCl in the injection brine on recovering additional oil, (ANDRADE, 2017) carried out core-flooding tests varying the concentration of NaCl in the water injected. To achieved that, they flooded the rock three different brines in order to observe any additional recuperation of oil; the sequence of each test is shown in Figure 31.

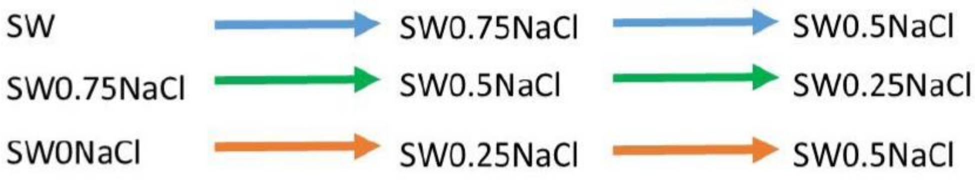


Figure 38 - Sequence of the tests performed (NaCl reduction). Source: (ANDRADE, 2017)

After the experiments, they noticed that the sodium chloride reduction in the injection brine could improve the oil recovery as it can be seen in Figure 39, which shows an increment in the oil recovery of 2.14% only by reducing in 25% the NaCl in the injection brine.

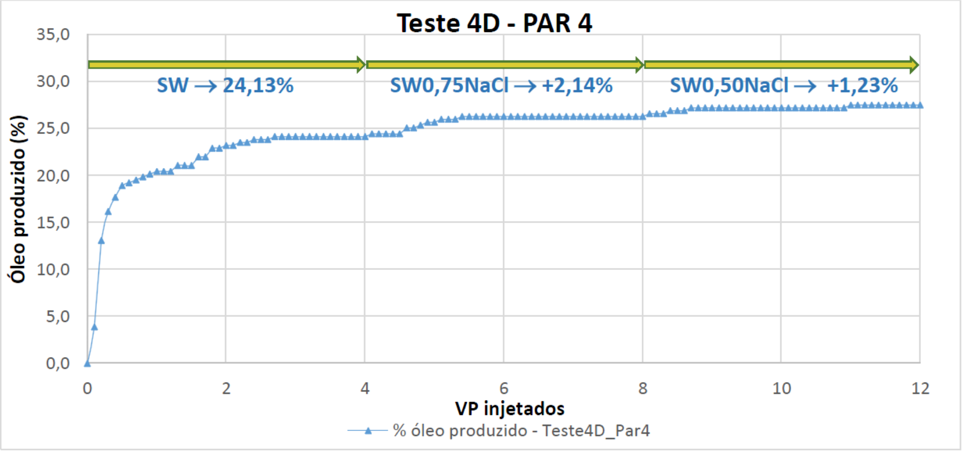


Figure 39 – Oil recovery versus porous volumes injected, effect of NaCl reduction. Source: (ANDRADE, 2017)

In the end, it can be seen that reducing the non-active ions in the injection brine can enhance the oil recovery in carbonate rocks, also (ANDRADE, 2017) concluded that the injection brine with the best performance is with a reduction of 25% in the NaCl. Figure 40 illustrates that this water can recover 34.2% by itself, which shows that this concentration of sodium chloride has the best performance in this sequence of the test.

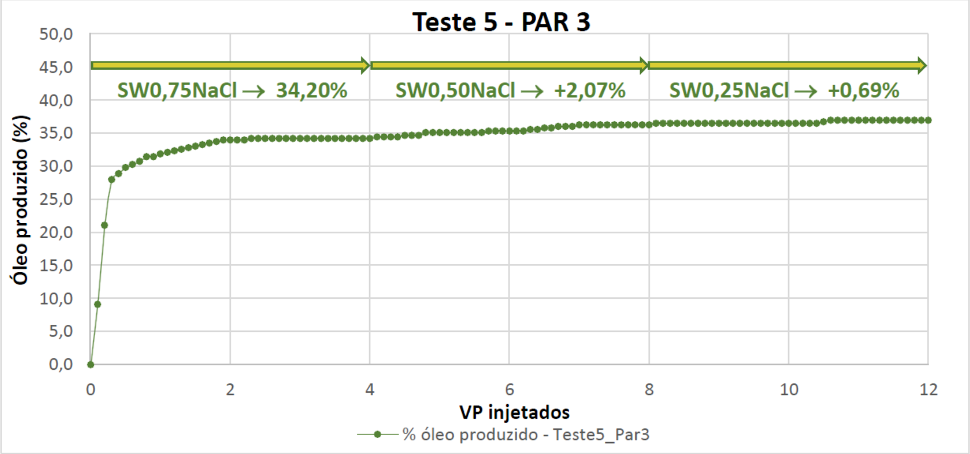


Figure 40 – Oil recovery versus porous volume injected, effect of NaCl reduction. Source: (ANDRADE, 2017)

3. MATERIALS AND METHODS

This chapter presents the description of material and methods applied in order to mimic the reservoir scenario in a lab environment. This section present in a logical order the preparation of the injection brines, live oil, core characterization, core preparation, and experimental set-up. Moreover, contain the results of oil characterization, and petrophysical properties.

3.1. Fluid preparation

3.1.1. Synthetic brines

Seawater (SW) can have different salinities depending on where is taken. Brine used in this work has a salinity of 40.363 part per million (ppm) and a component concentration as is shown in Table 2.

Table 2 - Seawater composition

Components	g/L
NaCl	23,4721
$CaCl_2$:$2H_2O$	1,4669
$MgCl_2$:$6H_2O$	10,5508
KCl	0,7245
$SrCl_2$:$6H_2O$	0,0396
Na_2SO_4	3,9165
TDS(mg/L)	34483

Synthetic seawater (SW) and its dilutions (SW $_{(x2)}$, SW $_{(x10}$, SW $_{(x50)}$, SW $_{(x100))}$) were used to perform the core flooding tests, Repsol-Sinopec Brazil provided the composition of Seawater.

In addition, formation water (FW) was provided and mimic initial water in the reservoir as well as simulating initial water saturation, similar to the reservoir conditions. Composition and concentration of salts that are in the FW are summarizing in Table 3.

Table 3 - Formation water composition

Component	g/L
NaCl	206,8191
KCl	7,5155
$MgCl_2:6H_2O$	15,1986
$SrCl_2:6H_2O$	7,8719
$CaCl_2:2H_2O$	30,9670
LiCl	0,1580
$BaCl_2:2H_2O$	0,0280
KBr	1,1027
Na_2SO_4	0,0991
TDS(mg/L)	241491

Preparation of seawater and formation water followed the following steps:

1. Use a 1000 ml volumetric flask for mixing 800 ml of deionized water with the salts, following the top to bottom order. The Sodium sulphate (Na_2SO_4) needs to mix firstly in a different volumetric flask with 100 ml of deionized water in order to avoid salt precipitation.

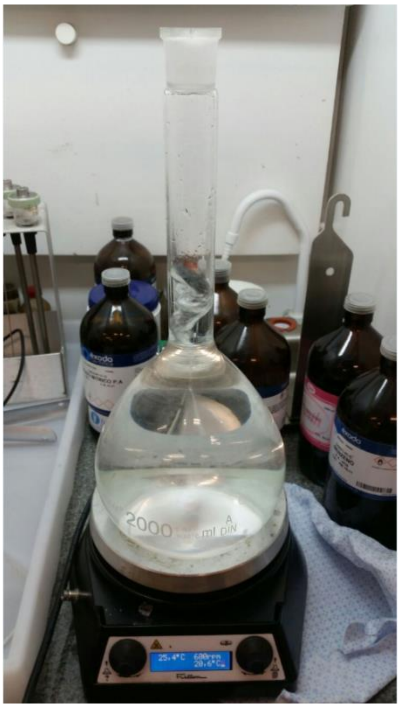


Figure 41 - Mixing salts

2. Once completing the salts dissolution process in both volumetric flasks both liquid were mixed with the other solution of salts during 30 minutes as shown in Figure 41.
3. Filter the brine solution using a 0.22 micrometres filter and a borosilicate filter in a vacuum system to remove the possible presence of contaminant particles, as illustrated in Figure 42.

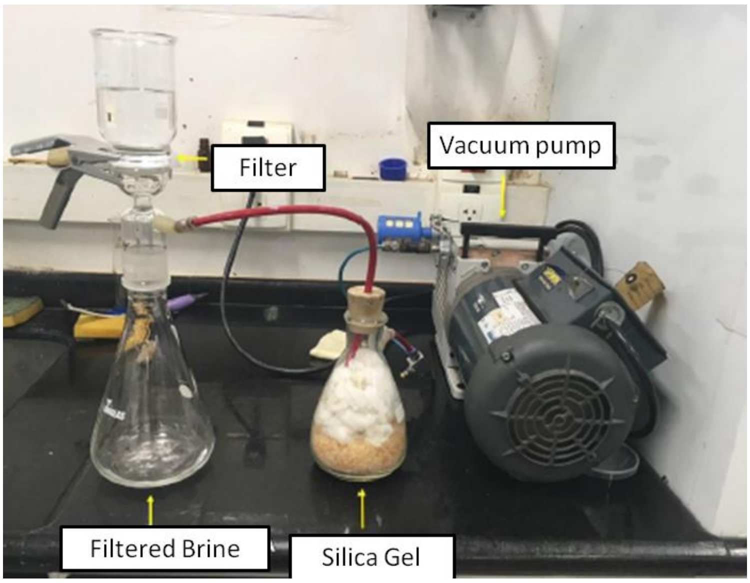


Figure 42 - Brine filtration process

4. After the filtration process concluded, an air removal procedure was carried out with the brine placed in a Kitassato flask and connected to the vacuum pump for 15 minutes, as shown in Figure 43.

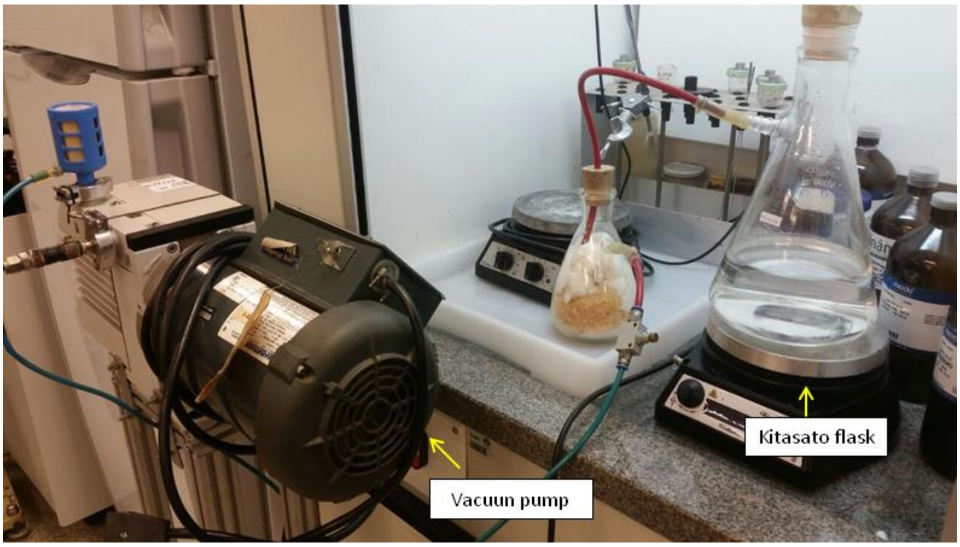


Figure 43 - Brine air removal process

3.1.2. Oil sampling

The oil used in these tests has come from a Pre-Salt field in Brazil. In order to homogenize the oil contained in the gallon where it was received it was necessary to heat it up to reservoir temperature and shake it each hour during 8 hours.

Then, oil was filtered with a 10μm filter to remove any sand or solids that are present in the oil. Figure 44 illustrates a schematic of the filtration set-up.

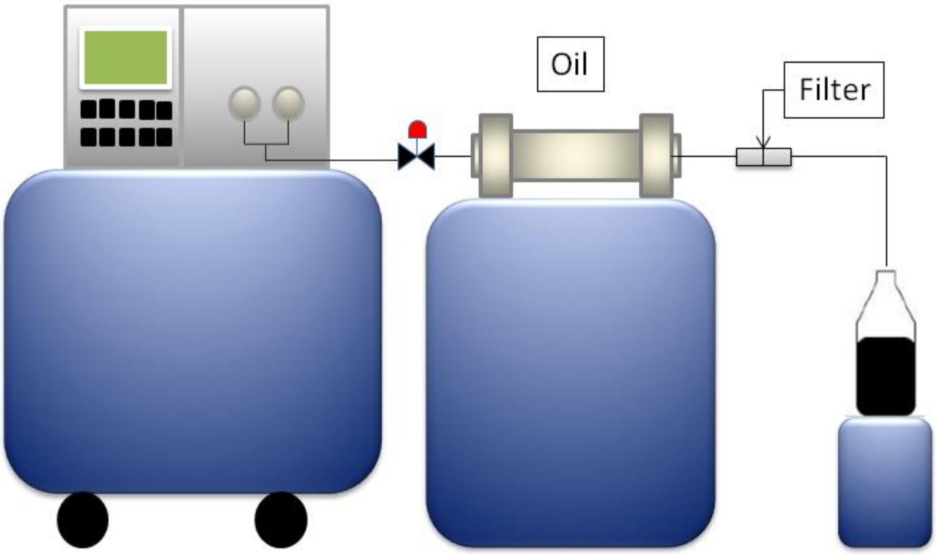


Figure 44 - Oil filtration set-up

This crude oil was used in the saturation and aging stages. After the aging process, recombined oil was prepared in order to replace the aging oil before running the test.

3.2. Oil characterization

There are different techniques for characterizing oil. The technique of saturated, aromatic, resins and asphaltenes (SARA) is the most used in the characterization of hydrocarbons, consisting of the separation of the oil in four fractions. The acid number determination procedures based on ASTM D-664 while the SARA separation technique on the ASTM D6560-12 and ASTM 2007-11 standard references. Table 4 illustrates the results of SARA and Acid number tests.

Table 4 - SARA and acid number of dead oil

SARA results	
Saturated (%)	79,73
Aromatics (%)	5,35
Resins (%)	14,27
Asphaltenes (%)	0,64
Acid number (mg KOH /g)	0,044

3.2.1. Density measurement

The measurement of dead oil density was performed with the help of Anton Paar's DMA-4500 *Density Meter*, shown in Figure 45. The fluid target (water or oil) is introduced into a U-shaped borosilicate glass cell, which is set to vibrate at a characteristic frequency. This frequency will change depending on the density of the fluid. The densimeter will precisely determine this characteristic frequency and, by mathematical conversion, the density of the fluid can be measured, compared to the frequencies encountered when using two standard fluids.

3.2.2. Viscosity measurement

Viscosity measurements of dead oil were made in a *Viscopro 2000 Cambridge viscometer*, shown in Figure 45. Its operation based on an electromagnetic concept. Two coils move a piston up and down magnetically at a constant force. Based on the frequency with which the piston completes the round-trip motion the viscosity of the fluid is calculated. The temperature of the fluid in the viscometer is continuously measuring with a temperature detector located at the base of the chamber. Since the viscosity of a fluid varies drastically with temperature, it is essential to know precisely the temperature in the measuring cell of the viscometer.

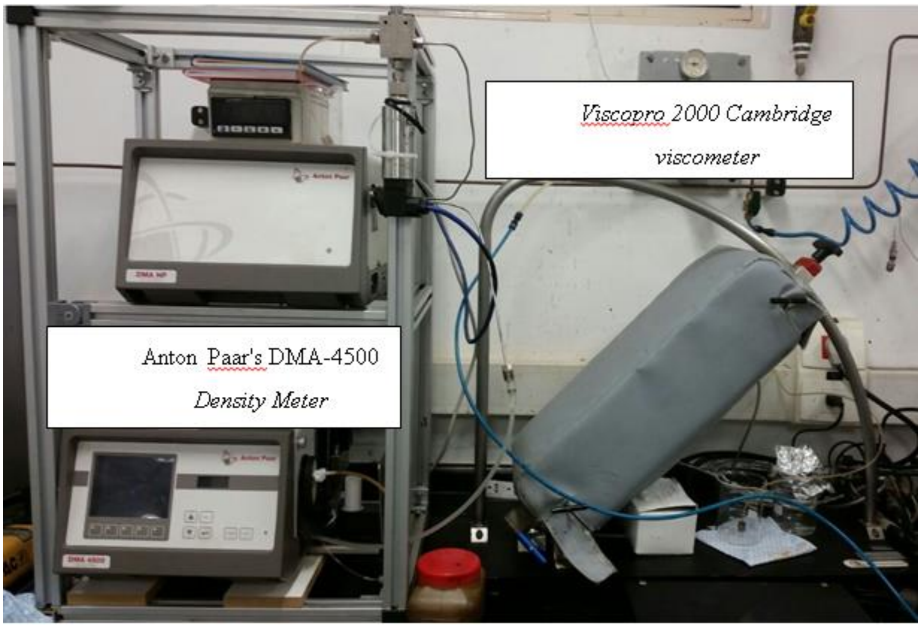


Figure 45 - Anton Paar's DMA-4500 Density Meter and Viscopro 2000 Cambridge viscometer

3.2.3. Live oil preparation

In order to mimic the reservoir conditions, it is necessary to reply oil under reservoir conditions. It is necessary to know the composition of the gas that is associated with the oil produced. The oil company provides the composition of the gas (CO_2 + C1 – C5) as well as basic crude oil properties such as RGO, °API density and viscosity. The composition presented in *Table 5* is the composition of the gas used to simulate live oil. However, this composition is a simplification of the real composition of the fluid in the reservoir.

Table 5 - Gas composition

Component	Atmospheric Gas (mol%)
CO_2	12.66
N_2	0.46
C1	71.9
C2	7.19
C3	4.91
n-C4	2.88

Knowing the RGO it is possible to calculate how much gas is in the crude at standard conditions. Then, with the gas composition, it calculated at laboratory condition. After knowing the volumes of gas and oil necessary to replicate the crude, they place in a single vessel in order to mix, and then, with a positive displacement pump, the mixture pressure is raised 500 psi above the bubble point pressure. When the reservoir pressure reached, DBR pump settled in constant pressure mode in order to keep constant pressure. Finally, the mixture will be stirred mechanically while an electrical resistance during 24 hours heats it up to the reservoir temperature. Table 6 illustrate the oil properties at reservoir conditions.

Table 6 - Oil properties at reservoir conditions

RGO ($\frac{m^3 std}{m^3 std}$)	265.13
Viscosity (cP)	0.79
Density (g/cm^3)	0.72

3.3. Cores characterization

The cores used in this work came from a reservoir in Brazil. The cores selected should meet three requirements. Firstly, they should be from the wells that are close between them than with others, and they are producer and injector, respectively. Secondly, cores must not have fractures, preferential flow paths or vugs, therefore, they were analysed by taking images in a Computer Tomograph scanner in order to select the core plugs with the best characteristics. Finally, the porous volume (VP) of the core or pairs selected must have a porous volume greater than 10 cm^3 and gas permeability (Kg) similar, the core data is in Table 7.

Table 7 - Core properties

Test Number	Pair number	Swi (%)	VP (cm^3)	Kg (mD)
1	Par 1	18	21.14	83.93
2	Par 5	26	16.93	27.68
3	Par 2	33	10.43	20.93
4	Par 4	34	15.13	31.80
5	Par 6	38	12.10	27.68
6	Par 7	31	13.41	34.30

3.3.1. Permeability measurement

Permeability was also determined in order to classify and select the samples for water-flooding experiments. All cores were measure with a permeabilimeter *Gas Permeameter* of *Core Laboratories, Inc (*Figure 47*)*. The equipment obtains the permeability of the rock by injecting nitrogen with a constant gas ratio and measuring the differential pressure of the core, then, using *Darcy's* equation to determinate permeability values.

In addition, other permeability measurements were made to the rock pair, this time with water flowing through the cores, it was applied the same concept above described. Using a DBR pump, constant water flow was settled-up, then, with a differential pressure transducer was collecting data from the cores and with Darcy's equation calculated the permeability. Figure 46 shows a scheme for permeability measurements.

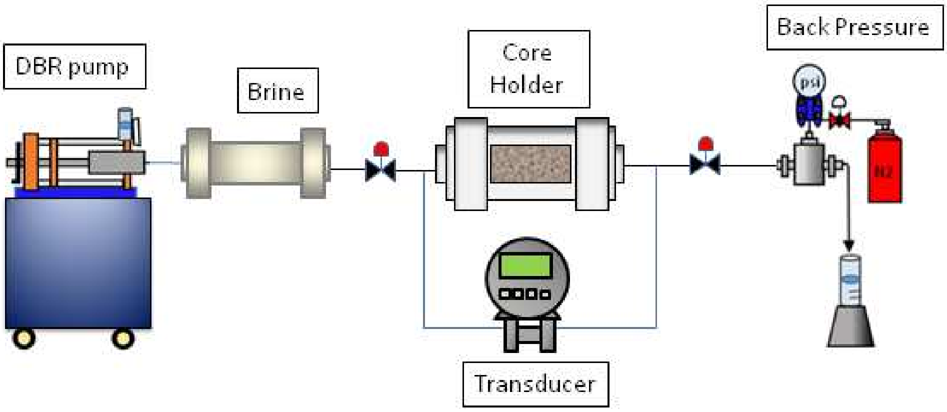


Figure 46 - Scheme for permeability measurement

3.3.2. Porosity measurement

Porosity measurements were performed in the core samples after the cleaning and drying procedures. These measurements were carried out in order to characterize the initial porosity for classification and samples for waterflooding experiments. All porosity measures were conducted in *Gas Porosimeter* of *Core Laboratories, Inc*, (Figure 47) using nitrogen and the porosity calculation is based in the Boyle´s law double-cell method that allows calculating porous volume.

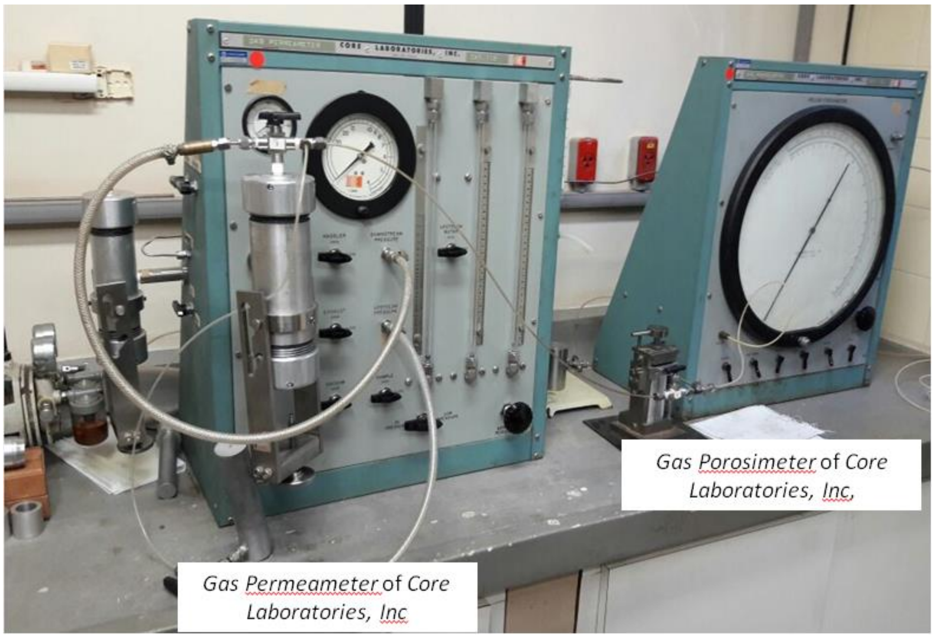


Figure 47 - Gas Permeameter of Core Laboratories, Inc and Porosimeter of Core Laboratories, Inc

3.3.3. Tomography

The selection of homogeneous core samples was carried out with a medical tomography Siemens model SOMATOM Spirit (Figure 48). The procedure consists of scanning cores samples to identify fractures or preferential flood channels. Then, according to the result of this screening, the pairs of cores were chosen for the next steps.

Figure 48 - Siemens Somatom Tomography

3.4. Core preparation

3.4.1. Core cleaning

After each test, the samples were cleaned in order to perform duplicates or using other brine schemes. Using a Soxhlet apparatus all cores were adequately cleaned, Figure 49. This equipment uses the solvent (acetone) flow in an intermittent process. The solvent vapor travels to the condenser, which makes it liquid. Thereafter, the condensed solvent moves to the chamber where the sample stayed. This chamber will slowly fill with hot solvent, and the compounds dissolve in the fluid. When the chamber of the Soxhlet is almost full, the solvent returns by siphon effect to the distillation flask along with the impurities of the rock. The cycle will repeat until the solvent appears to be clear.

Figure 49 - Soxhlet equipment

3.4.2. Core saturation with formation water

After petrophysical characterization, pairs of samples settled in a steel cell and evacuated for approximately 24 hours to remove the air from the porous space of the rock. Then, the cores samples saturated with formation water in a vessel at a constant pressure of 2000 psi for more 24 hours. A gauge measures the pressure in the hydraulic pump line to keep constant and monitor the pressure during the saturation process. Then, each pair was flooded with four porous volume of formation water to ensure 100% of water saturation as shown in Figure 46.

3.4.3. Core saturation with oil

Each pair of core plugs was settled up core-holder with a thermal blanket at reservoir temperature. The overburden pressure kept at 1000 psi with a DBR pump while the system temperature stabilized. The dead oil in a stainless steel vessel at a controlled temperature with the help of a thermal blanket as well. Then, dead oil is injected at the rate of 0.1 cm^3/min in the core plugs until there is no more water production, approximately four porous volumes (PV). The water produced after the injection of oil is collected and quantified and with the porous volume of the pair could be calculated the irreducible water saturation

(Swi); Table 7 presents the values of Swi of each core pair. Figure 50 shows a scheme of oil saturation.

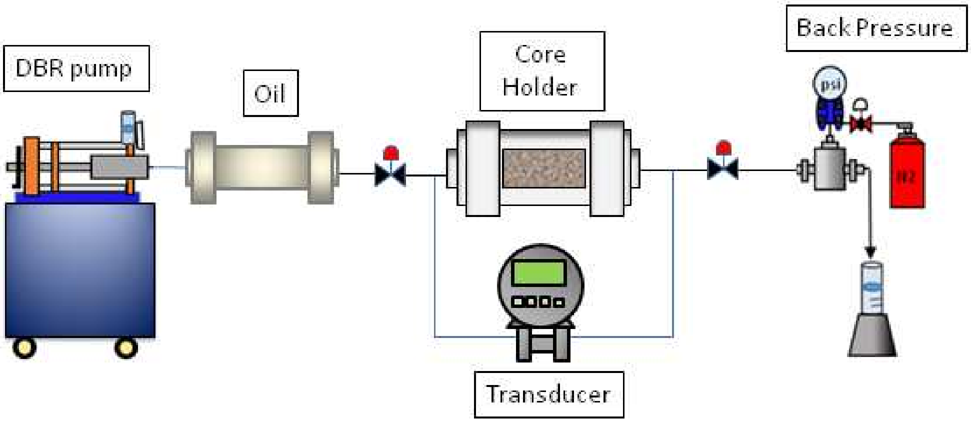


Figure 50 - Scheme of oil saturation

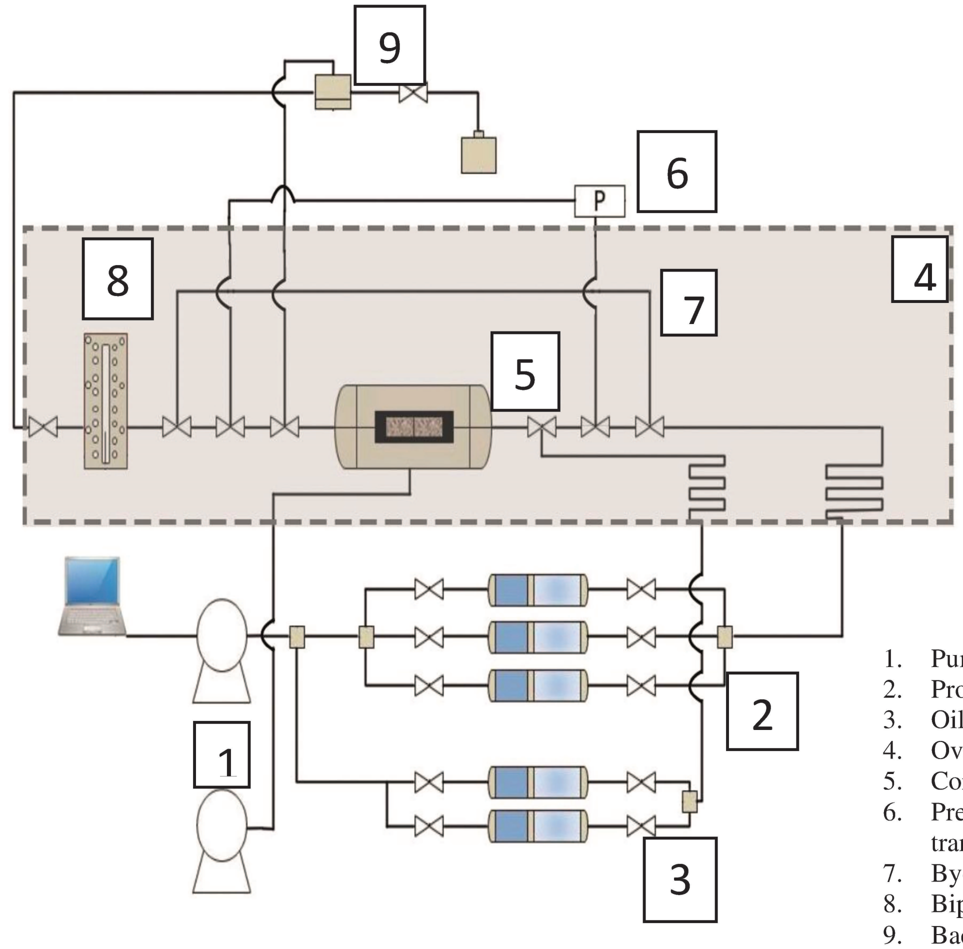
3.4.4. Wettability restoration

In order to achieve the wettability of the carbonate rock reservoir, an aging procedure is required. This procedure aims to obtain the wettability of the core material previous contact to drill fluid and cleaning process. The samples, in this case, must be aged for a fixed time (minimum time of 14 days) (FATHI; AUSTAD; STRAND, 2010) in a reservoir oil container called the aging cell Figure 51 under reservoir temperature and atmospheric pressure.

Figure 51 - Aging cell

3.5. Experimental set-up

Figure 52 shows the apparatus used for the core-flooding tests. The device comprises the following equipment: Positive displacement pump, accumulators, core-holder, oven, pressure transducer, backpressure system, valves, and biphasic separator. The live oil pre-prepared and stored in the accumulator and makes part of the oil saturation manifold. The reservoir plugs are placed in the core-holder after being covered with aluminium foil and thermoplastic sleeve to protect the Viton sleeve from potential damage caused by CO_2 present in the live oil. A biphasic separator installed to collect the oil produced at reservoir pressure and avoid the separation of gas. Two lines for the pressure transducer are connected in the input and output of the core-holder to measure and records the pressure drop during the test. The backpressure valve keeps the work pressure in the system.



1. Pumps
2. Production manifold
3. Oil change manifold
4. Oven
5. Coreholder
6. Pressure drop transducer
7. By-pass
8. Biphasic separator
9. Back-pressure valve

Figure 52 - Schematic waterflooding laboratory setup

3.5.1. Biphasic separator

In order to measure oil production at reservoir conditions and avoid the separation of gas from oil, it was necessary separator equipment able to work under high pressure and temperature. To accomplish it, an upgrade of a previous design of Petrobras was done. Figure 53 illustrates the final version of the separator; this equipment can work under extreme conditions of pressure and temperature (10000 psi and 124°C) allowing the laboratory of miscible method (LMMR) to explore new horizons in the recuperation of oil in carbonates.

Figure 53 - Biphasic separator

3.5.2. Dead volumes

In order to calculate more accurately the time of production of oil as well as the production, the dead volume (oil in the set-up lines that can contribute to inaccurate measurements) must be calculated. To achieve it, all lines were filled with water then, they were drained in test tubes to measure the volume.

Measurements of dead volumes in the lines of oil substitution were not necessary because along this stage data collection of volumes was not necessary.

3.5.3. Oil substitution

Before the tests, it is necessary to replace the dead oil that was saturating the core sample with the recombined oil. Five porous volumes were flooded with a DBR pump at a flow rate of 0.2 cm^3/min to guarantee the replacement of the dead oil. This procedure was carried out under test conditions.

4. RESULTS AND DISCUSSIONS

In this chapter presents the results of core-flooding experiments performed throughout the master. Results of oil recovery by reduction of total salinity and reduction of sodium chloride in the injection brine. Each experiment consists in the injection of three different slugs of modified seawater into the reservoir cores plugs to compare the performance of each slug in oil recovery. Besides, it presents results of ionic chromatography analyses carried out to the effluents collected after the injection of modified waters; these results will be available only for the last experiment of the series three and the replicates.

4.1. Total salinity reduction

Three tests carried out in order to evaluate the effect of reducing the total salinity of seawater in oil recovery of carbonate reservoir rocks, three tests looking for the best performance and a replicate of the experiment with the best performance to verify the results. Figure 54 shows the sequence of the tests performed.

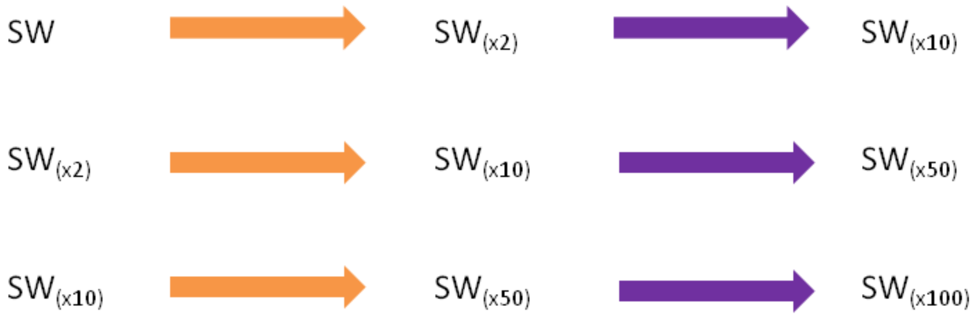


Figure 54 - Sequence of tests for total salinity reduction.

The first test of the sequence one was designed to study the effect of reducing total salinity, starting with seawater (SW) as a secondary mode followed by seawater two times diluted (SWx2), and finally, seawater ten times diluted (SWx10). Figure 55 illustrates the cumulative oil recovery regarding original oil in place (OOIP) and the pressure drop in the core sample for the injected brines.

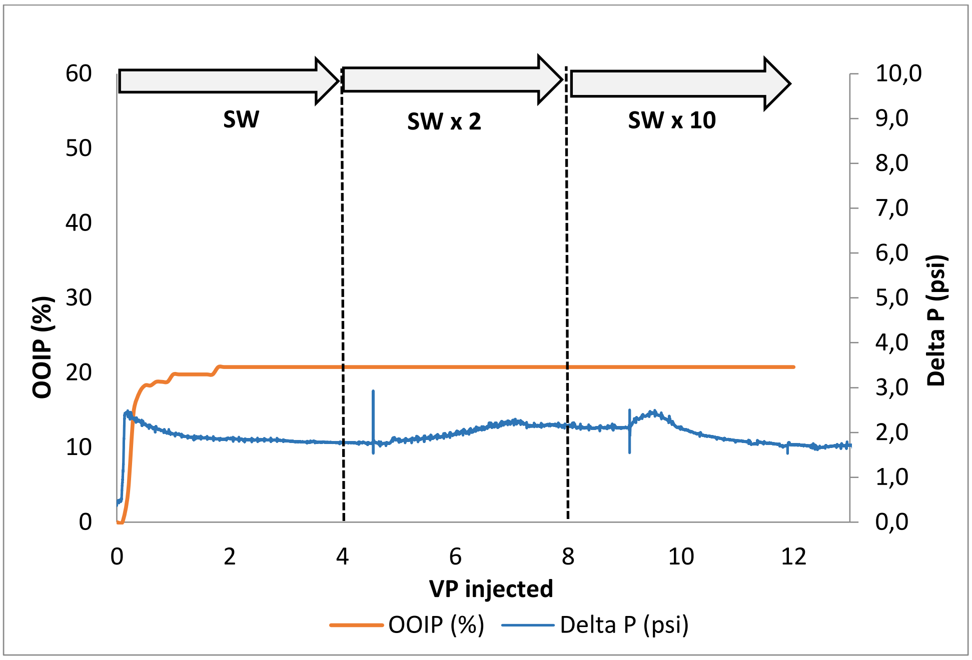


Figure 55 - Oil recovery and pressure drop versus pore volume injected, first test.

The oil produced by the injection of seawater was 20.7 % of OOIP; this slug represents a secondary oil production. Figure 55 shows that no additional oil was produced after the injection of the diluted slugs (SWx2 and SWx10) respectively. Therefore, reduction of the total salinity did not show improvements in the oil recovery.

The pressure drop curve shows a couple of interesting facts; the first one is the increase in the differential pressure when seawater two times diluted (SWx2) is injected; that increase can be associated with precipitation of some salts or carbonate minerals in the porous media causing damage in the rock permeability and therefore injectivity lost. However, with the injection of seawater ten times diluted (SWx10), the permeability rises to slightly higher values of the initial permeability; dissolution of the previously precipitated mineral in the porous media is a hypothesis that could explain this phenomenon. Figure 56 shows the behaviour of effective water permeability throughout the test. It is important to point out that the most accurate value of permeability is where it is partially stable.

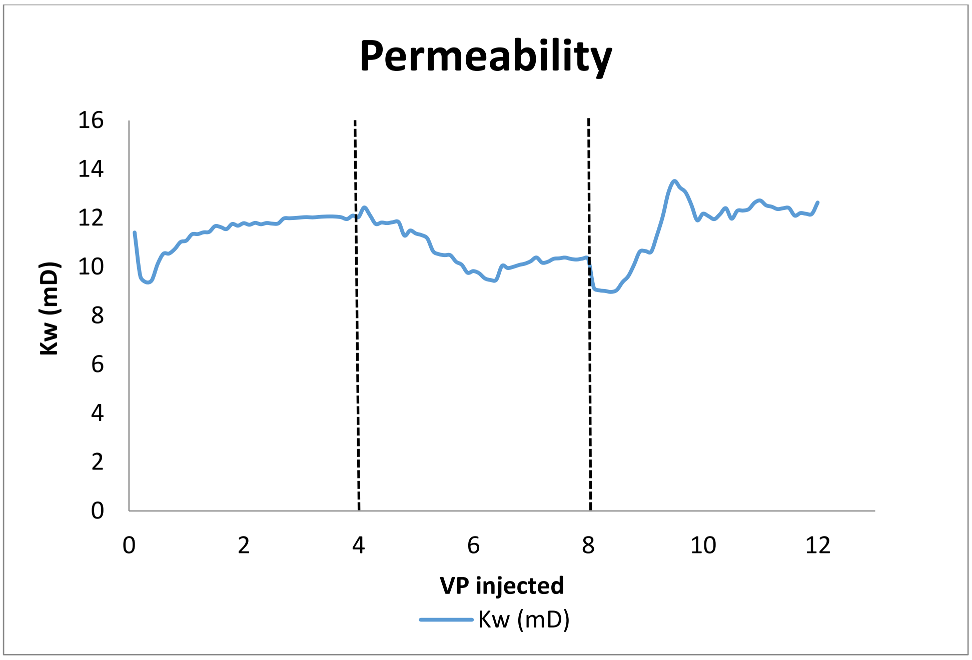


Figure 56 - Effective water permeability versus porous volumes injected, first test.

The results of oil recovered in this first experiment (20.7% of OOIP) can be compared with those obtained by (ANDRADE, 2017). They obtained an oil recovery of 21.08% of the OOIP in dolomites by the injection of seawater in a secondary stage (Figure 32), those results show repeatability, and it can say that the oil recovery by the injection of seawater would be around 20 to 25% of the OOIP. On the other hand, our results do not show and additional oil recovery by the injection of SWx2 and SWx10, while Figure 32 shows additional oil recovered by the injection of diluted forms of seawater ($SW_{(x2)}$, and $SW_{(x10)}$),1.65%, and 3.63%, respectively. This additional oil can be attributed to the difference in rock mineralogy, while (ANDRADE, 2017) used dolomite rocks, we used real reservoir rock which has more complex mineralogy probably affecting with this the performance of the technic.

The second core-flooding test used seawater two times diluted (SWx2) as secondary oil recovery followed by seawater ten times diluted (SWx10) in tertiary mode, and fifty times diluted (SWx50) as a ultimate mode, respectively. Figure 57 illustrates the cumulative oil recovery regarding OOIP and the pressure drop in the core sample for the injected brines.

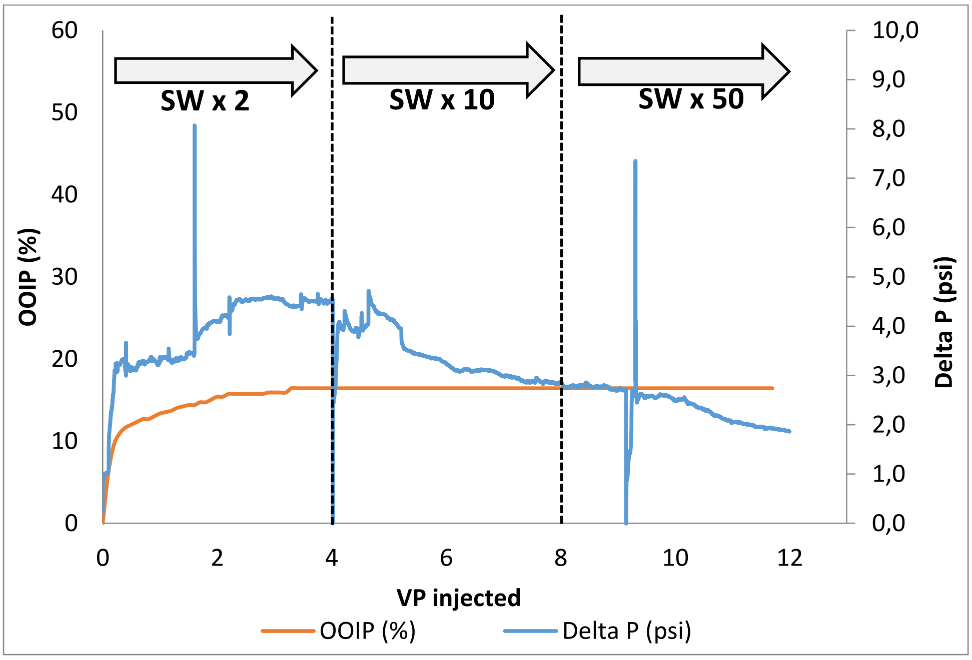


Figure 57 - Oil recovery and pressure drop versus pore volume injected, second test.

The oil produced by the injection of seawater two times diluted was 16.4% of OOIP; this slug represents a secondary oil production. Figure 57 shows that no additional oil was produced after the injection of the diluted slugs (SWx10 and SWx50) respectively. Therefore, reduction of the total salinity did not show improvements in the oil recovery. In addition, total oil recovery by using SWx2 in a secondary stage is lower than oil recovery by SW in a secondary stage. It is important to point out that the oil recovered by the SWx2 is the lowest, coinciding with the behaviour of the pressure drop in the previous experiment when the permeability of the porous media was affected negatively.

The pressure drop curve shows that after started injecting the SWx10 the differential pressure started to drop leading to an increase in the permeability; SWx50 times shows the same trend than SWx10. The most reliable theory to explain this behaviour in the differential pressure is the dissolution of the porous media. Figure 58 shows the behaviour of effective water permeability throughout the second test.

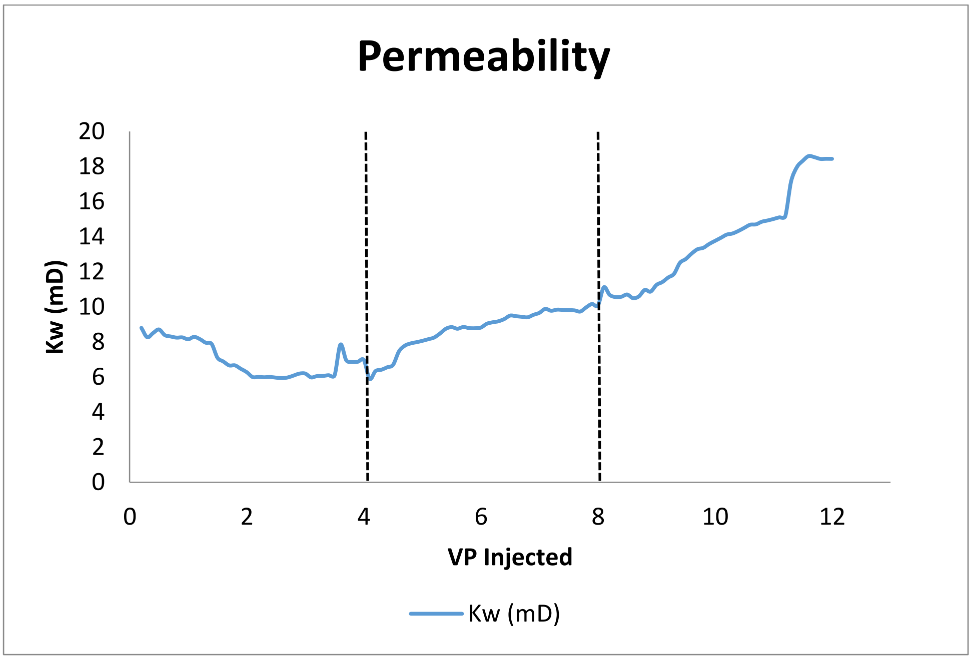


Figure 58 - effective water permeability versus porous volumes injected, second test.

The third experiment consisted in the injection of seawater ten times diluted (SWx10) as a secondary oil recovery followed by the injection of seawater fifty times (SWx50) and hundred times diluted (SWx100) respectively. The goal of this experiment is first; evaluate the reduction of total salinity in oil recovery as well as the performance of SWx10 in a secondary stage.

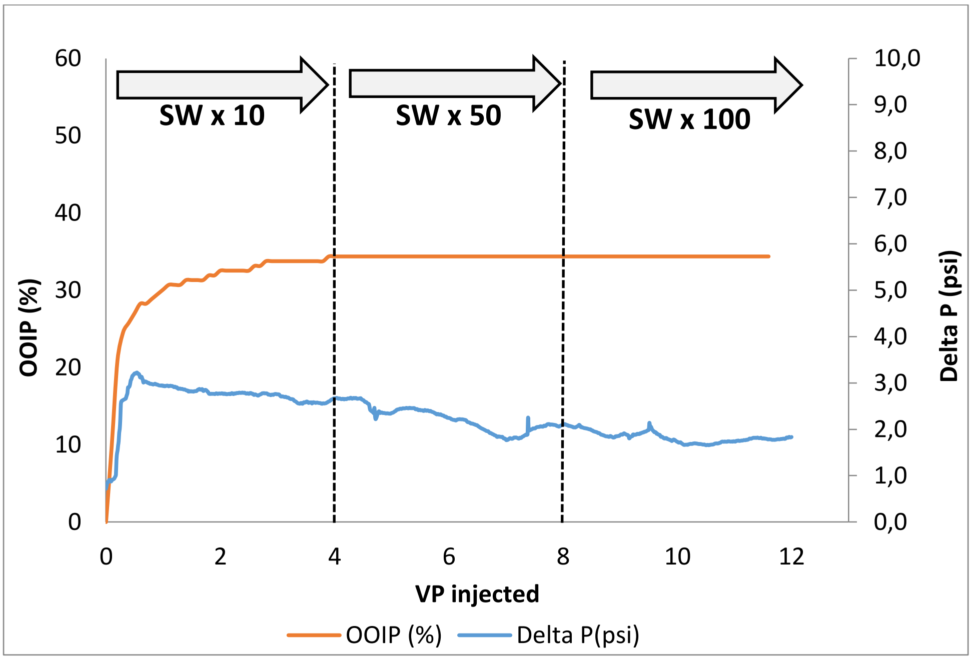


Figure 59 - Oil recovery and pressure drop versus pore volume injected, third test

The oil produced by the injection of seawater ten times diluted was 33.7 % of OOIP; this slug represents a secondary oil production. The performance of SWx10 is by far the best of the three experiments. The injection of SWx50 recovered 0.65% at the beginning of the injection; however, we cannot conclude that this additional oil recovery is due to the injection of the SWx50 slug. To sum up, the total oil recovery in this test was 34.3%, which is a good performance, compared with the previous test. Figure 59 illustrates oil recovery and differential pressure throughout the test. The pressure drop curve shows a decreasing trend when the injection brine diluted ten times or more, indicating dissolution of the porous media leading to an increase in the permeability of the rock. However, this behaviour is not enough to confirm that this phenomenon is occurring. It is necessary to analyse the effluents of the injection brine in order to see if there is a variation in the concentration of the ions. In the following sections, ionic chromatography results analysis will give us a better understanding of what is going on in the porous media due to the fluid-rock interaction.

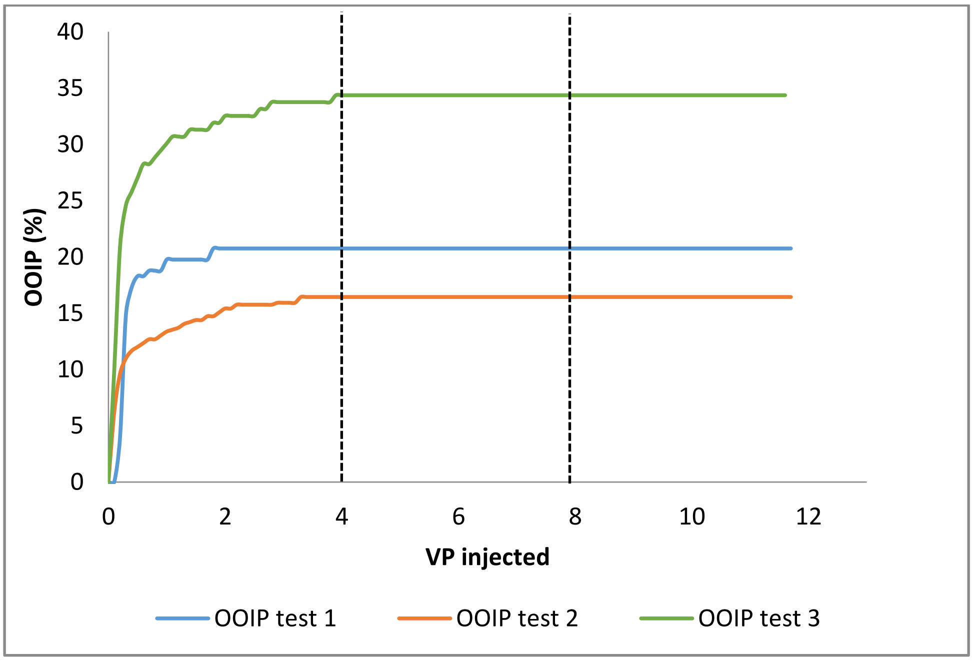


Figure 60 - Oil recovery versus porous volumes injected

The results obtained in this experiment can be compared with the results of (ANDRADE, 2017), who obtained 31.62% of the OOIP recovered by the injection of seawater ten times diluted, which was the best result obtained by them. Therefore, can be pointed that the seawater diluted ten times has the best results in both works.

Figure 60 shows the oil recovery in each test, to sum up; SWx10 obtained the best oil recovery with 33.75 % of the oil in place. The worst oil recovery was with SWx2 in a secondary method, and it matches with the only brine that leads to a decrease in the permeability.

4.2. Sodium chloride reduction

This section presents the results of NaCl reduction in the injection brine (seawater). Figure 61 illustrates the sequences designed to evaluate the effect of reducing NaCl in the injection brine in oil recovery of carbonate reservoir rocks.

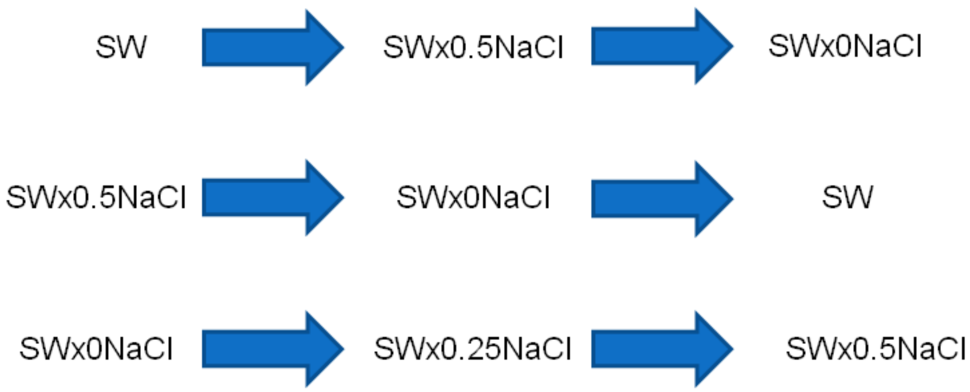


Figure 61 - Sequence of tests for NaCl reduction

The first test of the sequence two designed to study the effect of reducing NaCl, starting with seawater (SW) as a secondary method followed by seawater depleted 50% in NaCl (SWx0.5NaCl), and finally, seawater without NaCl (SWx0NaCl). Figure 62 illustrates the cumulative oil recovery regarding OOIP and the pressure drop in the core sample for the injected brines in the left axis, while in the right axis represents the pressure drop in the rock throughout the test.

The oil produced by the injection of seawater was 25.33 % of OOIP; this slug represents a secondary oil production. Figure 62 shows that no additional oil was produced after the injection of the slugs depleted in NaCl (SWx0.5NaCl and SWx0NaCl) respectively. Therefore, NaCl reduction did not show improvements in the oil recovery in a third and ultimate stage of production.

Comparing this result with the first test of series one, the oil recovered by the seawater is comparable in both case, as we can see in Figure 55 and Figure 62.

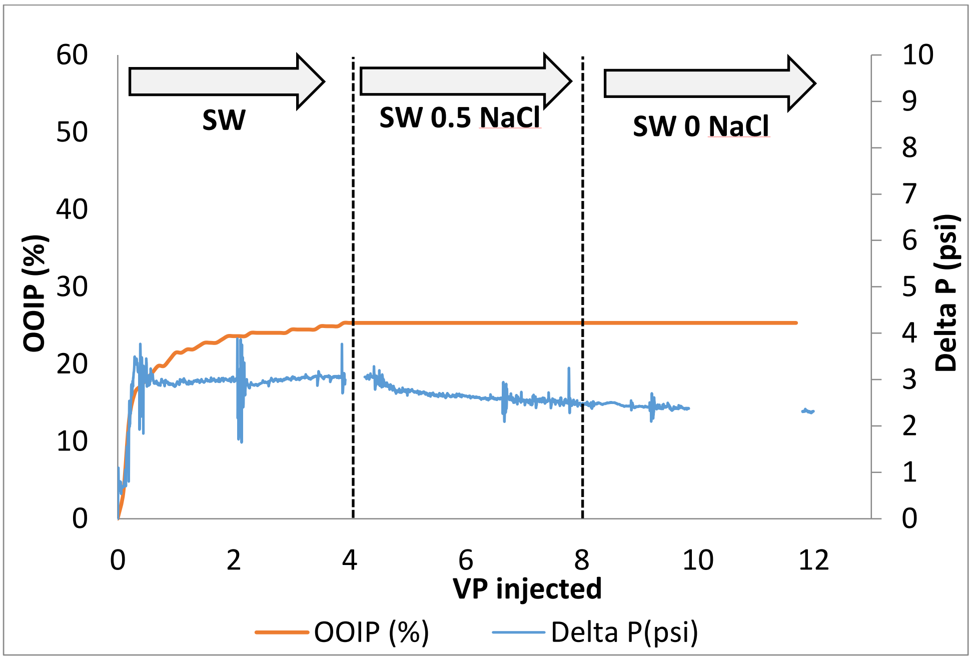


Figure 62 - Oil recovery and pressure drop versus pore volume injected, fourth test

The pressure drop curve shows a decreasing trend after stared injecting brines depleted in NaCl. During this test occurred problems with the collection of pressure drop data, however still can see that the curve tends to drop. This tendency of the pressure drop curve when water depleted in seawater was injected indicates dissolution in the porous media.

The fifth core-flooding test used seawater 50% depleted in NaCl (SWx0.5NaCl) as secondary oil recovery followed by seawater without NaCl (SWx0NaCl), and seawater (SW) as an ultimate method, respectively. Figure 63 illustrates the cumulative oil recovery regarding OOIP in the left axis and the pressure drop in the core sample for the injected brines in the right axis.

The oil produced by the injection of seawater 50% depleted in NaCl was 35.43% of OOIP; this slug represents a secondary oil production. Figure 63 shows that no additional oil was produced after the injection of the other slugs (SWx0NaCl and SW) respectively. Therefore, this indicates that both, NaCl reduction and increase did not show improvements in the oil recovery in the tertiary and ultimate stages. The pressure drop curve did not show any relevant behaviour referring to dissolution process occurring in the rock, it only shows and slight increase when started the injection of seawater.

The results of this experiment have an oil production comparable to the third test of the series one, where injected SWx10 recovered 33.75% of the OOIP. However, in this experiment the behaviour of the pressure drop is entirely different, while in the third test of the series one the pressure drop curve tends to drop with the injection of diluted seawater indicating dissolution of the porous media, in the test five this behaviour is not present, however, the oil recovery is very similar. Therefore, this indicates that the principal mechanism acting when diluted seawater was injected could be the dissolution of the porous media while reducing NaCl concentration the mechanisms could be an ionic exchange.

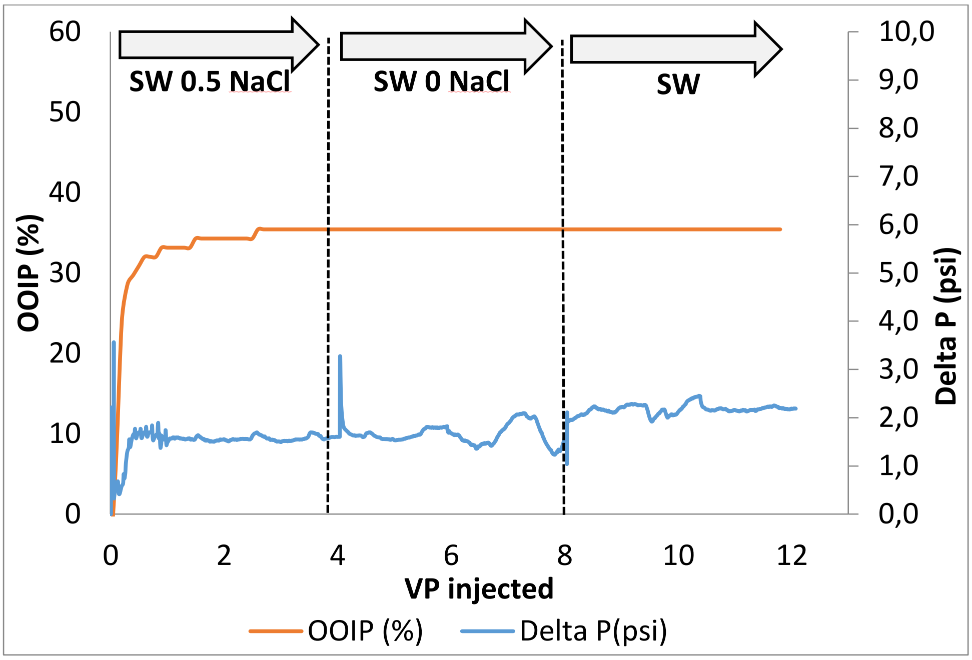


Figure 63 - Oil recovery and pressure drop versus pore volume injected, fifth test

The last core-flooding test of the series 2 used seawater without NaCl (SWx0NaCl) as secondary oil recovery followed by seawater with 25% of NaCl (SWx0.25NaCl), and finally, seawater depleted 50% in NaCl (SWx0.5NaCl) as an ultimate method, respectively. Figure 64 illustrates the cumulative oil recovery regarding OOIP in the left axis and the pressure drop in the core sample for the injected brines in the right axis.

The oil produced by the injection of seawater depleted entirely in NaCl was 53.68% of OOIP; this slug represents a secondary oil production. Figure 64 shows that no additional oil was produced after the injection of the other slugs (SWx0.25NaCl and SWx0.5NaCl) respectively. Therefore, increasing NaCl in the injection brine did not show improvements in the oil recovery in the tertiary and ultimate stages.

The behaviour of pressure drop curve in this experiment is similar with the curve showed in Figure 7 obtained by (YOUSEF et al., 2010) who conclude that dissolution of the porous media occurred when seawater injects diluted seawater.

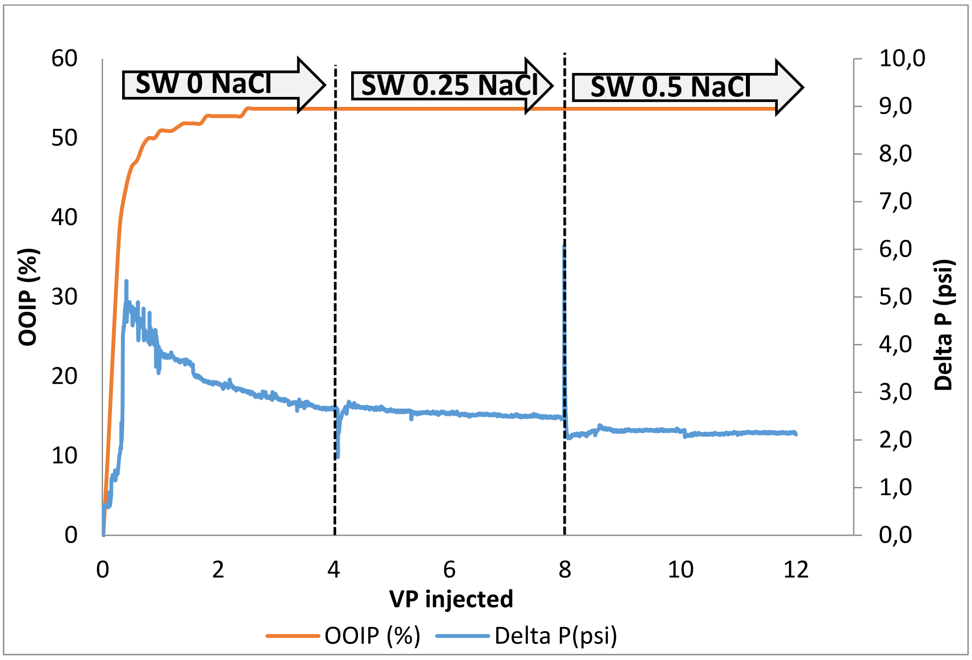


Figure 64 - Oil recovery and pressure drop versus pore volume injected, sixth test

Even though it was not additional oil recovery after the first water slug injection, there is an increase in the oil recovered by the reduction of NaCl in the injection brine. Figure 65 illustrates clearly how the oil recovery was affected positively by the reduction of NaCl. While the oil recovered by the injection of seawater is approximately 25% with seawater, without NaCl is 53%.

Finally, a replicate of the sixth experiment was performed. The scope of this last core-flooding test was to replicate and confirm results of the last experiment of the series two, which was the best result obtained along the development of this work in a different core plug. Therefore, it was used seawater without NaCl (SWx0NaCl) as secondary oil recovery followed by seawater with 25% of NaCl (SWx0.25NaCl), and finally, seawater depleted 50% in NaCl (SWx0.5NaCl) as an ultimate method, respectively. Figure 66 illustrates the cumulative oil recovery regarding OOIP in the left axis and the pressure drop in the core sample for the injected brines in the right axis.

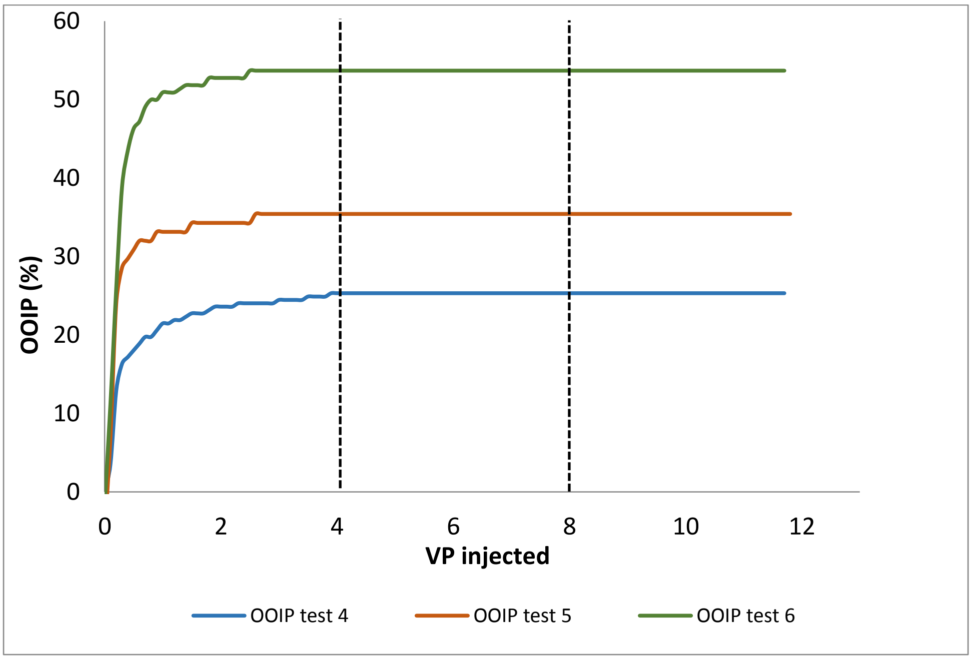


Figure 65 – Oil recovery versus porous volumes injected

The oil produced by the injection of seawater depleted entirely in NaCl was 59.38% of OOIP; this slug represents a secondary oil production. Figure 66 shows that no additional oil was produced after the injection of the other slugs (SWx0.25NaCl and SWx0.5NaCl) respectively. Therefore, it confirms again that increasing NaCl in the injection brine did not show improvements in the oil recovery in the tertiary and ultimate stages.

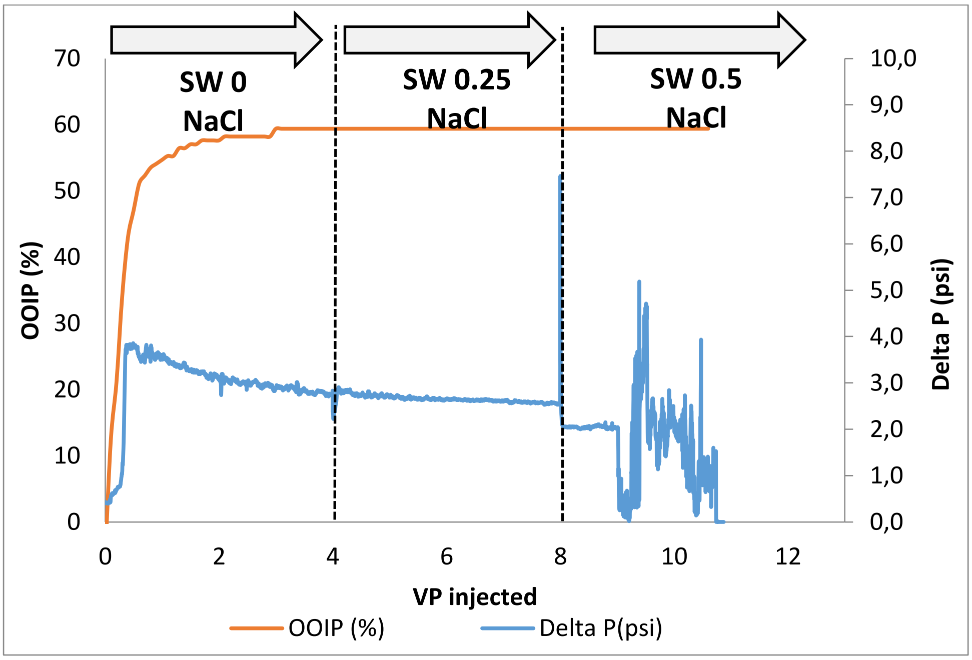


Figure 66 - Oil recovery and pressure drop versus pore volume injected, seventh test. Replicate of the sixth test, same water sequence with different rock

The oil produced by the injection of seawater without NaCl in both experiments (six and seven) have a significant production of oil, 53.68%, and 59.38% respectively (Figure 67). Therefore, it helps to confirm that the injection of water that would have the best performance would be SWx0NaCl. The behaviour of pressure drop curve in this experiment matched almost perfectly with the pressure drop curve of test six as we can see in Figure 67, making think that the rocks might be the same formation.

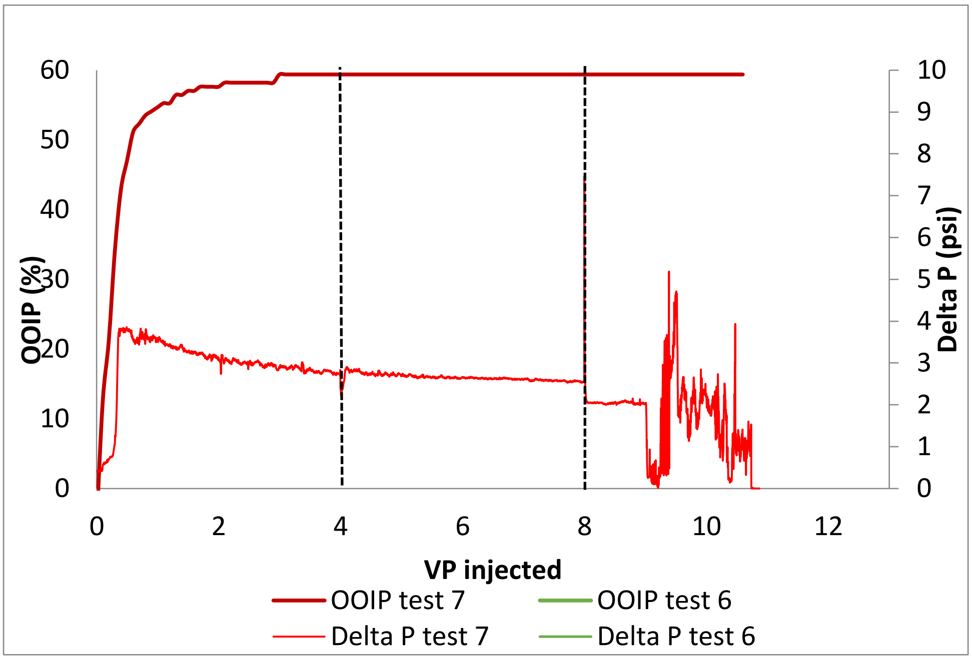


Figure 67 - Oil recovery versus porous volumes injected. Comparison between test sixth and seven

4.3. Ionic chromatography

Ionic chromatography analysis made in the effluents of the sixth experiment gave some clarity about the role that the ions are playing, and the interactions between the water injected and the rock. As pointed out in the previous sections, two kinds of ions play an essential role in the wettability alteration of carbonate rocks. First, the active ions (sulphate, magnesium, and calcium), who are responsible for wettability alteration by the interaction between them and the rock's surface. Secondly, there are the non-active ions (sodium, and chlorine), who difficult the interaction between the active ions with the rock. Therefore, an analysis in the quantity of these ions can give us an idea of the interaction between the rock and the ions present in the water injected, for example, if they are staying attached to the rock surface, indicating with this, ion exchange mechanisms. On the other hand, the concentration of calcium is a reliable indicator of dissolution of the porous media if the concentration of this ion increase after it went through the rock sample.

Figure 68 shows the concentration of magnesium throughout the test. The graphic does not show any relevant variation in the concentration of the ion. Therefore, magnesium is not interacting with the rock, which is coherent with (ZHANG; TWEHEYO; AUSTAD, 2007) who observed that at high temperature the ion magnesium could substitute Ca^{2+} from the rock surface and the rate of substitution is directly proportionate with the temperature.

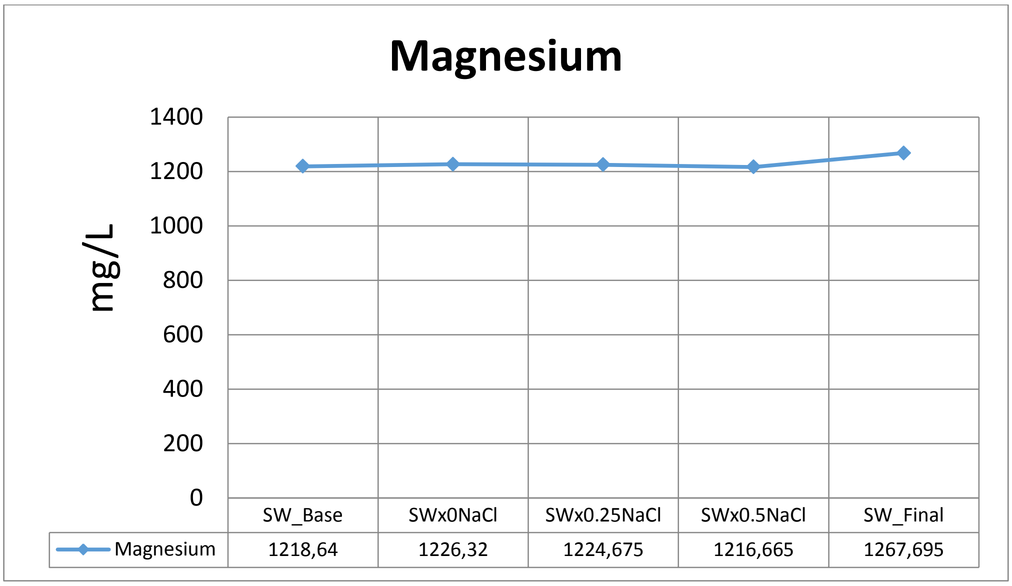
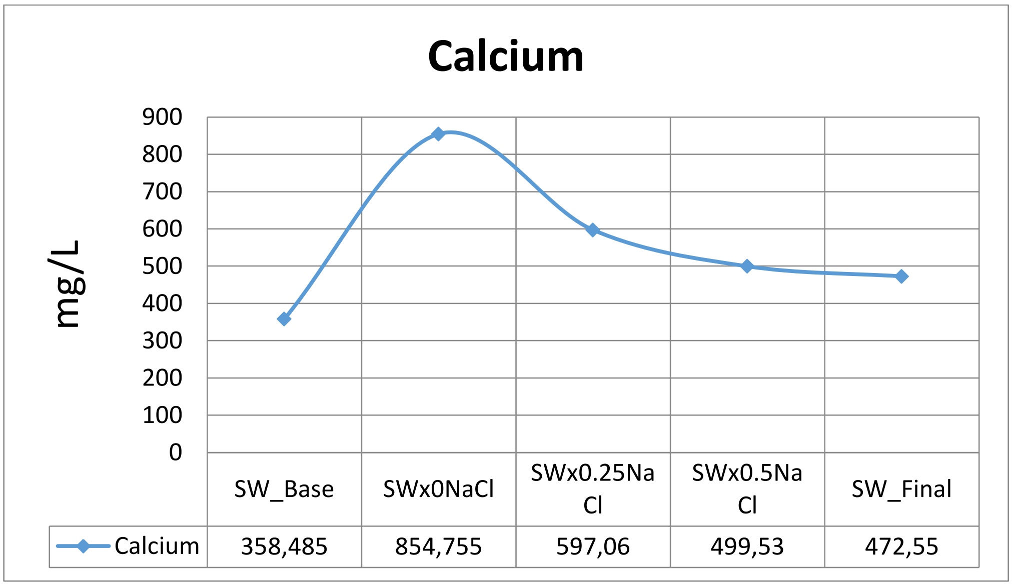


Figure 68 - Concentration of ion magnesium versus brine injection

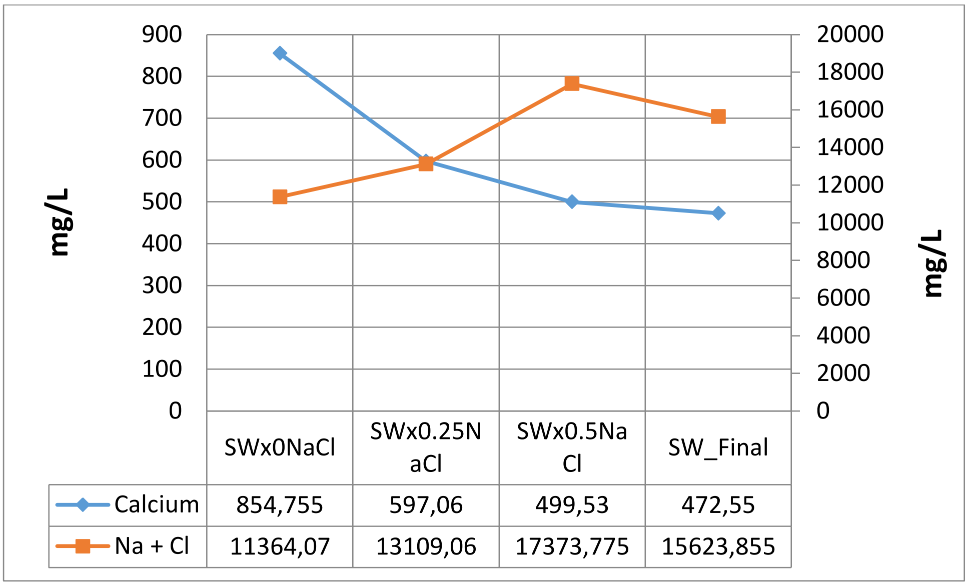
The concentration of calcium in Figure 69 shows an increase in the concentration of the calcium ion after the injection of SWx0NaCl, and then it starts to decrease when NaCl was added to the injection brine water. This result together which the behaviour of pressure drop curve in this experiment (Figure 64) gave strong indications of rock dissolution; therefore, dissolution mechanism is acting when injected SWx0NaCl as well as with other brines.



	SW_Base	SWx0NaCl	SWx0.25NaCl	SWx0.5NaCl	SW_Final
Calcium	358,485	854,755	597,06	499,53	472,55

Figure 69 – Concentration of calcium ion versus brine injected

However, the dissolution of the rock decrease when the concentration of sodium and chlorine increase. Figure 70 illustrates how the concentration of non-active ions affects the dissolution of the rock negatively, not only they do not let the active ions interact with the rock, they interfere with the dissolution of the rock. However, the fact that the increase of NaCl in the injection brine do not let the rock dissolution occur is more because of the ionic strength increases with the added of sodium chloride. Therefore, the brine cannot dissolve the rock. On the other hand, brine depleted in NaCl also loses its ionic strength, which could help it to rock dissolution.



	SWx0NaCl	SWx0.25NaCl	SWx0.5NaCl	SW_Final
Calcium	854,755	597,06	499,53	472,55
Na + Cl	11364,07	13109,06	17373,775	15623,855

Figure 70 – Calcium and sodium ion concentration versus injected brine

Figure 71 illustrates the concentration of calcium and magnesium ions in the injection brine before the test began (SW_base), during the test at the end of each slug injected (SWx0NaCl, SWx0.25NaCl, and SWx0.5NaCl), and at the end of the test from the biphasic separator (SW_Sep).

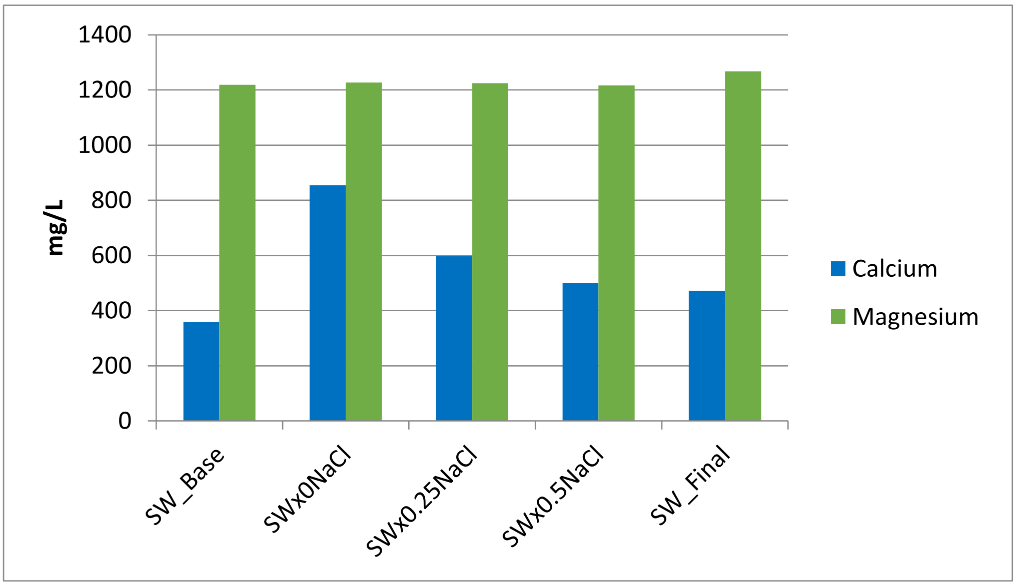


Figure 71 – Calcium and magnesium ions present in injection brine during the test

Ionic chromatography analysis made in the effluents of the seventh experiment gave some confirmation of the results obtained in the experiment sixth. However, some technical problems did not allow the collection of the effluent after the injection of the first water (SWx0NaCl).

Figure 72 shows the concentration of magnesium throughout the seventh test. The graphic does not show any relevant variation in the concentration of the ion. Therefore, magnesium dissolution is not occurring along the test. This results compared with the previously obtained in experiments sixth are congruent and show the same behaviour.

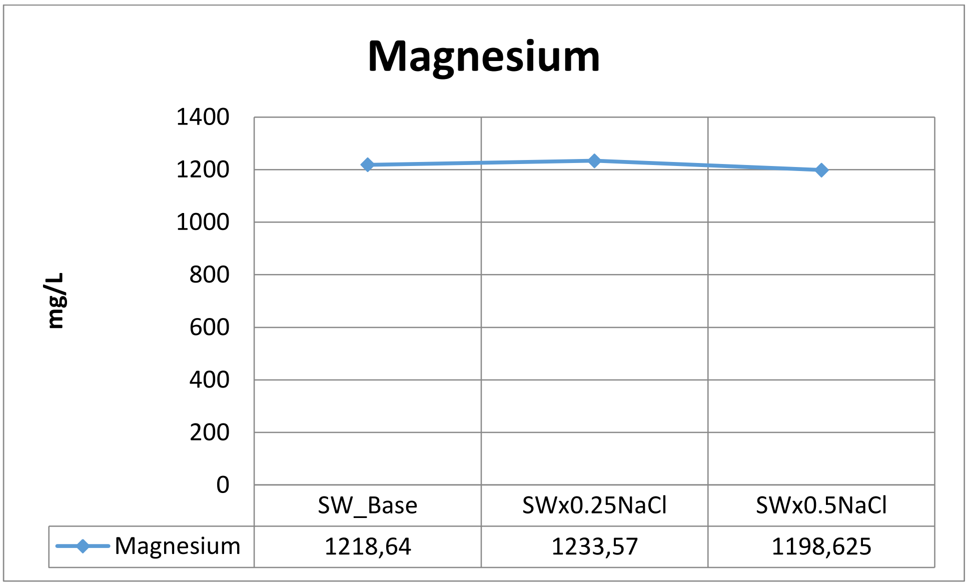


Figure 72 - Concentration of ion magnesium versus brine injection. Replicate of sixth test.

The concentration of calcium in Figure 73 shows an increase in the concentration of the calcium ion after the injection of SWx.25NaCl, and then it starts to decrease when NaCl was added to the injection brine water. This result together which the behaviour of pressure drop curve in the experiment seventh (Figure 66) gave strong indications of rock dissolution; therefore, dissolution mechanism is acting when water depleted in NaCl is injected into the reservoir.

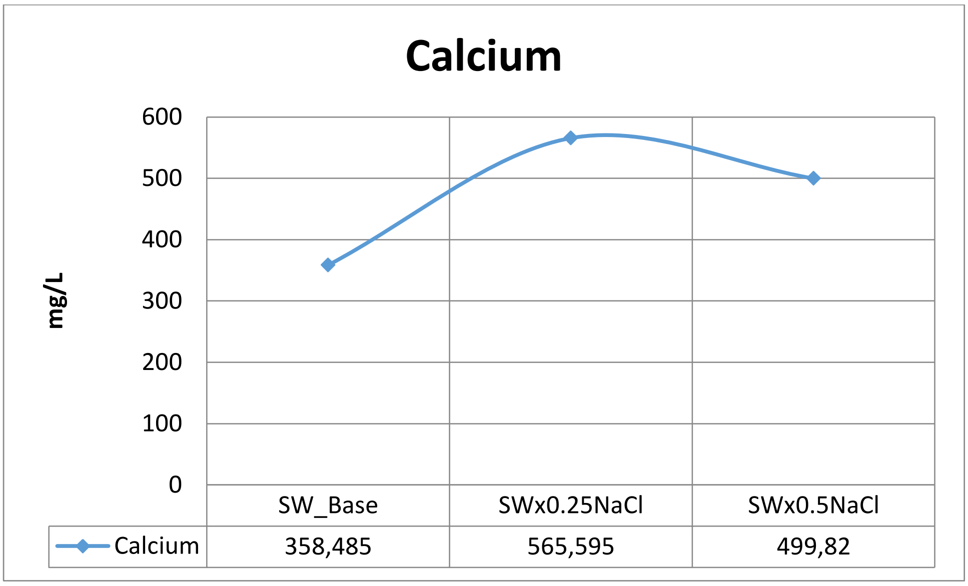


Figure 73 - Concentration of calcium ion versus brine injected. Replicate of sixth test

Figure 74 illustrates the concentration of calcium and magnesium ions in the injection brine before the test began (SW_base), after the injection of SWx0.25NaCl and SWx0.5NaCl.

Figure 74 - Calcium and magnesium ions present in injection brine during the test. Replicate of sixth test

5. CONCLUSION

This chapter presents the conclusions obtained by this work after of evaluating the potential of injecting seawater and its modifications (reducing total salinity and NaCl) into carbonate rocks.

- Analysing the impact of reducing the total salinity in the injection brine on the oil recovery of carbonate rocks, it can be concluded that, the injection brine that obtained the best oil recovery by reducing the total salinity reduction tests was the seawater ten times diluted (SWx10) with an oil recovery factor of 33.75%. These results coincide with previous works done in our research group.
- The experiments with sodium chloride reduction showed an inverse relationship between the quantity of Na^+, and Cl^- ions present in the injection brine and the oil recovery in carbonate rocks. The core-flooding tests illustrate that the reduction of NaCl can enhance the oil recovery factor by double if it compares injection brine without NaCl 53.68% of the OOIP with seawater 25.33% of the OOIP.
- Oil recovery for the tests of total salinity reduction was generally low compared with other works done by other reach groups. However, the reservoir conditions used in

this work were harsher as well as the mineralogy of the rocks used had an extreme complexity due to they were real reservoir rocks.

- The ion chromatography analysis shows an increment in the concentration of the ion calcium in the effluents, giving a strong indication of rock dissolution by injection of seawater depleted in NaCl.
- It was possible to develop an experimental apparatus that was able to work under reservoir conditions with a collection data system under the same conditions. This set-up will be the base of future researches at reservoir conditions.

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