RATE OF WETTABILITY ALTERATION BY CASPIAN SEA ENGINEERED WATER IN CARBONATE FORMATIONS

by

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Originality Statement

I, Meruyet Bazhanova, hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at Nazarbayev University or any other educational institution, except where due acknowledgement is made in the thesis.

Any contribution made to the research by others, with whom I have worked at NU or elsewhere is explicitly acknowledged in the thesis.

I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.

Signed on April 15th, 2020

ABSTRACT

Most carbonate reservoirs in the Caspian Sea region are heterogeneous and oil wet. The utilization of conventional water flooding does not usually result in significant incremental oil recoveries. Tuning the salinity and composition of the injecting fluid could alter the wettability towards the more water-wet state. The rate of alteration in crude oil-brine - carbonate rock (CBR) interactions such as wettability is a critical parameter to design the duration of the engineered water flooding for the field application.

Salinity and concentration of potential determining ions (PDI) such as Mg^{+2}, Ca^{+2}, and SO_4^{-2} in Caspian Sea water (CSW) affect the wettability during water flooding. In this work, carbonate rock samples were aged at 80°C to achieve the original natural/oil-wet conditions. The concentration of PDIs was adjusted in CSW injection brines. Characteristic experiments such as dynamic contact angle measurements, pH analysis, ion chromatography and spontaneous imbibition were applied to study the rate of alteration to more water-wet conditions by different samples of ion-engineered water. A methodology was developed to select the most effective treatment of CSW for secondary imbibition process.

Our studies showed that CSW with the salinity of 15,000 ppm is an efficient displacing fluid as it can initiate an engineered water flooding EOR process by changing the initial wettability of the rock from 86° to 35° within 2 days. The adjustment of salinity and concentration of active ions makes the multi-ion exchange (MIE) mechanism much faster. For example, with 5 times diluted CSW it was possible to achieve the same change in wettability only within 9-hrs. To achieve the optimum adjustment of CSW, the effect of dilution and active ions on the rate of MIE was measured. It was found that 20 times and higher dilutions of CSW were not effective in contact angle alteration as the concentration of potential determining ions (PDI) was decreased. Presence of Ca^{+2} and SO_4^{-2} ions simultaneously at an optimum concentration in 5 times diluted CSW was the most effective case which was able to shift the contact angle from 86° to 22° only within 9-hrs. Moreover, our lab experiments demonstrated that sulfate ions accelerate the wettability alteration process. pH and ion chromatography studies proved the effectiveness of MIE in this condition. Finally, spontaneous imbibition tests have demonstrated that the rate of oil production and ultimate oil recovery are twice higher with an optimum smart brine, that is in agreement with contact angle measurements.

The results obtained from this research work suggest that even a short period of interaction with optimized engineered water can affect the brine, oil, and carbonates interactions and change the reservoir rock initial wettability from neutral to strongly water-wet state. This allows to efficiently design engineered water flooding based on CSW in the field scale and make such projects more profitable.

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1 INTRODUCTION

1.1 Global energy demand

According to the International Energy Agency and BP statistical review of world energy, the global primary energy consumption in 2018 has increased noticeably since 2000 as depicted in Figure 1. This was mainly driven by population growth and improving living standards (IEA 2019). Figure 1 illustrates the energy consumption measured in terawatt-hours (TWh) per year. At the same time, demand for all fuels increased, especially for natural gas and crude oil. The oil and gas industry will remain to be a primary fuel source for many countries (BP Energy Outlook 2019). Applying conventional recovery processes only 30% of global oil reserves can be extracted. Moreover, more than half of the remaining oil is being trapped in carbonate reservoirs, because of their complex nature and their initial wettability state. (Petroleum Engineer`s Guide to oil field chemicals and fluids, 2015). Therefore, the economic significance and potential of enhanced oil recovery processes in carbonates are very high.

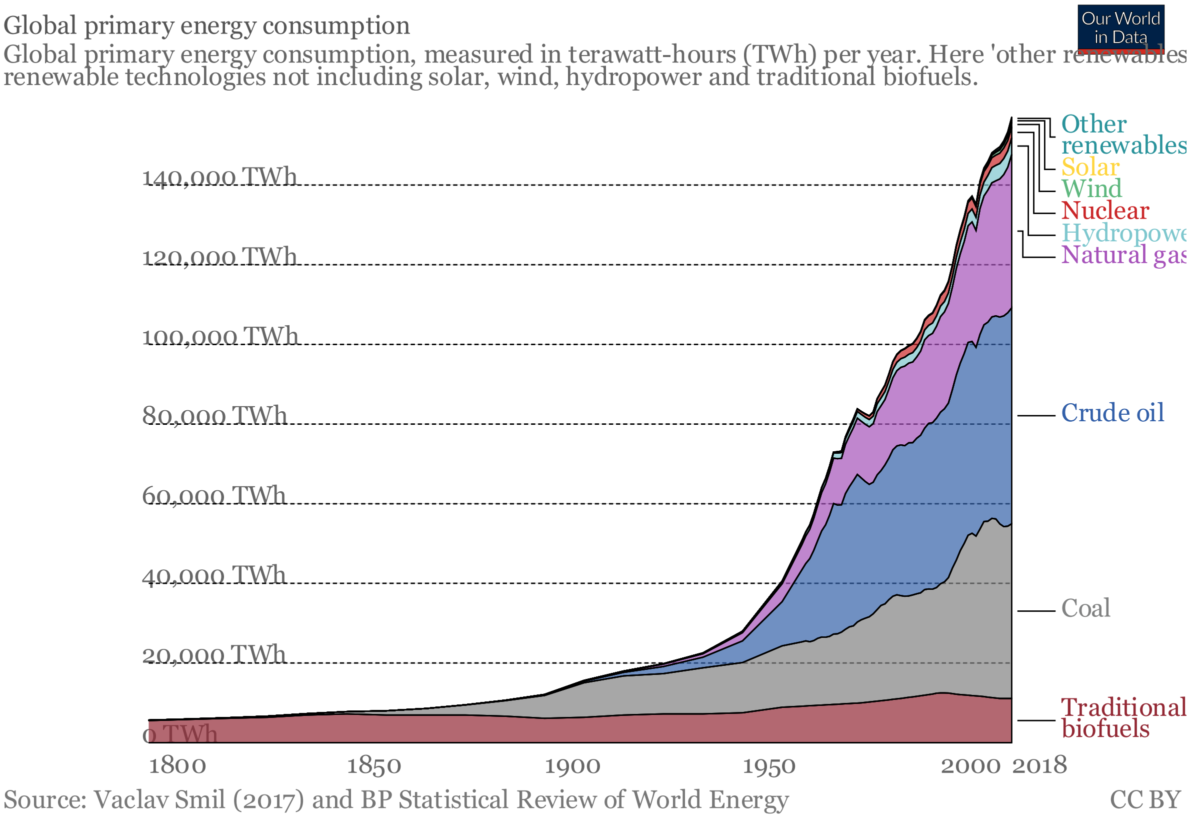


Figure 1. Global energy consumption (BP statistical review of world energy, 2017)

1.2 Oil recovery phases

In the first stage of petroleum production, hydrocarbons are usually produced under the natural energy, including oil & gas drive and gravity drainage, which happens due to pressure difference between the reservoir and bottom hole of the well. But in process of time, the oil production rate gradually decreases as the reservoir`s natural energy being depleted, while at the same time water starts to be produced with an increasing rate. Reservoir`s natural energy includes oil and gas expansion, gas drive and water drive, gravity drainage, etc. The first stage of hydrocarbon production which is based on the natural reservoir`s energy is called primary recovery or primary production. On average, during primary recovery it is possible to produce only 10 % of all oil initially in place (OIIP) (Economides, 2013) This is due to reduced reservoir pressure, or low and not economical oil production rate, or high water cut in wells.

In the early days of the oil industry, the produced formation water was disposed to the nearby rivers or other water resources. The first time when saline brine was accidentally reinjected into the well from which it was produced was applied in the Bradford oil field in Pithole city of Pennsylvania (US) in 1865. (Craig, 1971) As a result, later it became a common oilfield practice to use produced formation water for reinjection processes. Reinjection of water into the production zone of the well helps to produce additional oil left behind primary production after the reservoir`s natural energy has been depleted by displacement and pressure maintenance operations. This stage of hydrocarbon production is called secondary recovery or secondary production. Secondary recovery also includes gas reinjection normally into the gas cap zone. The successful application of secondary recovery processes allows producing about 15 – 40 % of OIIP or GIIP. After secondary recovery, there is still a substantial amount of oil that needs to be recovered. Applying special techniques such as thermal flooding, gas injection, or chemical flooding enables us to recover additional oil remained during the secondary recovery in the reservoir. This recovery process is referred to as a tertiary recovery process or enhanced oil recovery (EOR). (Economides, 2013)

1.3 Low salinity waterflooding in sandstones

Generally, waterflooding showed many positive results in oil fields by producing additional oil after primary recovery. As an example, by the 1970s many oil fields in the US, USSR, and China started to actively use waterflooding as an oil recovery strategy. During first waterflooding projects the best candidate for water was formation brine, as it is readily available and is compatible with the reservoir. Moreover, small capital investment and operational costs, ease of injection, its availability, nonnegative environmental impact, and several other factors contributed to the development of waterflooding as one of the most economical and effective methods for increasing hydrocarbon recovery. (Economides, 2013)

Starting from early waterflood projects, many attempts have been made to fully understand this technique. However, in the past, no one considered the quality of injected water. It was only treated out of solids and organic elements that can be reactive with underground crude oil, brine, and rock (CBR) system. The low salinity waterflooding (LSW) technique attracted much attention when Morrow with his research colleagues in 1991 performed several experiments to investigate the dependence of oil recovery and CBR interactions on the injected brine composition using Berea sandstone. (Jadhunandan, 1991) After this work, other researchers investigated and confirmed that injecting low salinity water into sandstone core samples can show positive results in terms of additional oil recovery during different laboratory tests. (Tang, 1999) A most accepted mechanism behind the low salinity phenomenon in sandstones is the wettability alteration of the clay minerals towards the more water-wet state. (Ligthelm D., 2009) Based on the positive response of LSW and due to its simplicity, it can be concluded that this method can be considered as a potential EOR method for sandstones, which can allow the production of an additional 5 – 20 % of OOIP. (Al-Shalabi, 2017) Nowadays, there are several merged research projects based on low salinity/smart waterflooding, such as “LoSalTM” trademark registered in 2005 by BP (Robertson, 2007); “Smart WaterFlood” by Saudi Aramco (Yousef et al., 2012); “Designer Waterflood” by Shell (Ligthelm D. J., 2009); and “Advanced Ion Management (AIM)” by ExxonMobil. (Gupta et al., 2011)

1.4 Low salinity and smart water flooding in carbonates

Low salinity/smart water flooding in carbonates became a new research trend when the first unexpected high oil recovery from the chalk reservoir at the Ekofisk field in the North Sea was produced. (Al-Shalabi E.W., 2017) This historical event attracted many researchers to this area, and different prospective have merged to fully understand the “smart water flooding” concept in carbonate reservoirs. Most of the research done on this topic summarizes the incremental oil recovery by optimization of brine salinity and ionic composition. However, few works still observed no or very little response of low salinity in some carbonates and sandstones. (Winoto et al., 2012) This section aims to review the main findings and summarize the results of the work performed on smart water flooding in carbonates.

The main difference between low salinity and smart waterflooding is that low salinity water is obtained just by dilution of formation brine using distilled water. Whereas to prepare smart water, we can change the overall salinity content and ion composition by dilution or by adding specific chemical components. In recent years extensive research has shown the importance of chemistry of the injected fluid into the reservoir; tuning salinity and ionic composition of the injected brine can affect initial CBR system`s condition by altering the wettability of the rock that overcomes capillary force trapping oil in the reservoir, changing residual saturations of the fluid, enhancing microscopic sweep efficiency and eventually improve the performance of waterflooding.

One of the best examples of utilizing smart water is a work done by Webb et al. in 2005. Webb with his colleagues in 2005 conducted two laboratory experiments at reservoir conditions using carbonate cores from the North Sea carbonate field (Valhall) to investigate the efficiency of low salinity water containing sulfate ions compared to formation simulated brine with no sulfate. The first experiment utilized a sulfate-free formation simulated water and the second one used seawater, which contains sulfate as a displacing fluid. The salinity content of formation water was 95500 ppm, while seawater contained 61700 ppm with SO_4^{-2} 2650 ppm. From the resultant data of capillary pressure curves by using seawater, it was able to achieve $S_{or} = 0.1$, while with formation water, $S_{or} = 0.14$. The results are presented in Figure 2.

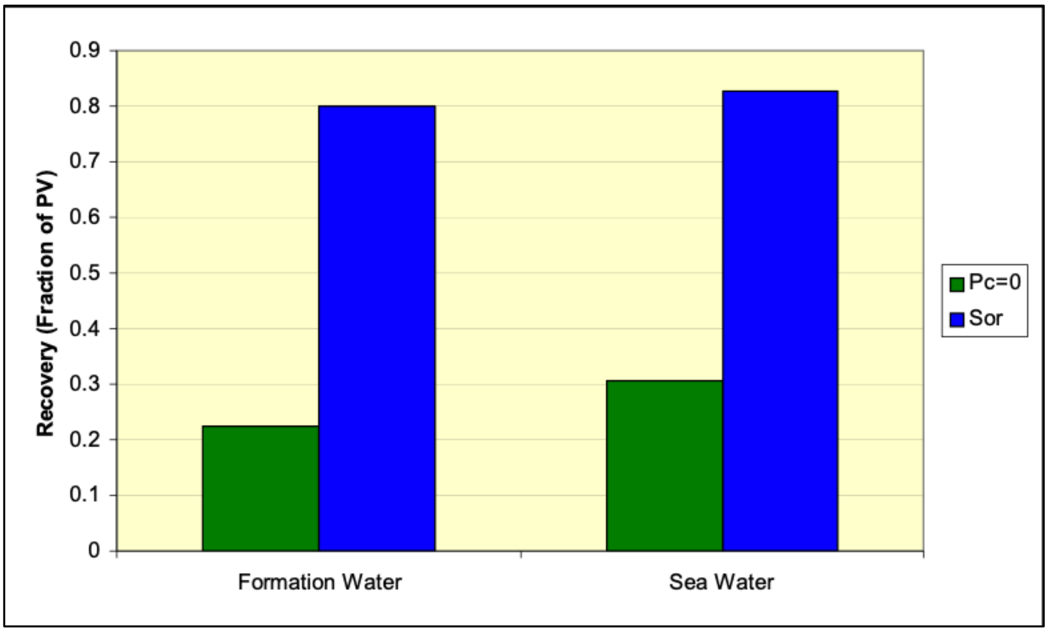


Figure 2. comparison of oil recovery by formation brine and sea water (Webb et al., 2005)

It can be concluded that seawater containing sulfate ions showed higher oil recovery compared to formation water with no sulfate ions. Finally, by comparing the saturation change in spontaneous imbibition tests between seawater and formation brine, the proposed mechanism was changing the wettability of the rock to a more water-wet state. (Webb et al., 2005)

In 2007, Zhang et al. studied wettability alteration based on the performance of spontaneous imbibition curves by adding different ions. As a result of their work, SO_4^{-2}, Mg^{+2} and Ca^{+2} were found to be potential determining ions (PDI), i.e. main contributors to wettability alteration towards the more water-wet state. It was suggested that to improve oil recovery sulfate ions should act together with either calcium or magnesium. Moreover, it was found that oil recovery is a strong function of temperature, the oil recovery increases with increasing temperature. However, at high-temperature, Mg^{+2} ions have a superior effect over Ca^{+2}. (Zhang, 2007)

The main objective of the research work conducted by Ligthelm and his group in 2009 was to investigate the effect of "designer waterflooding" on limestone cores from the Middle East at 60 °C by conducting spontaneous imbibition experiments. Three different brines were used: LS1 formation brine from an aquifer zone, LS2 modified formation brine by increasing sulfate content, and LS3 is a modified formation brine by reducing calcium content.

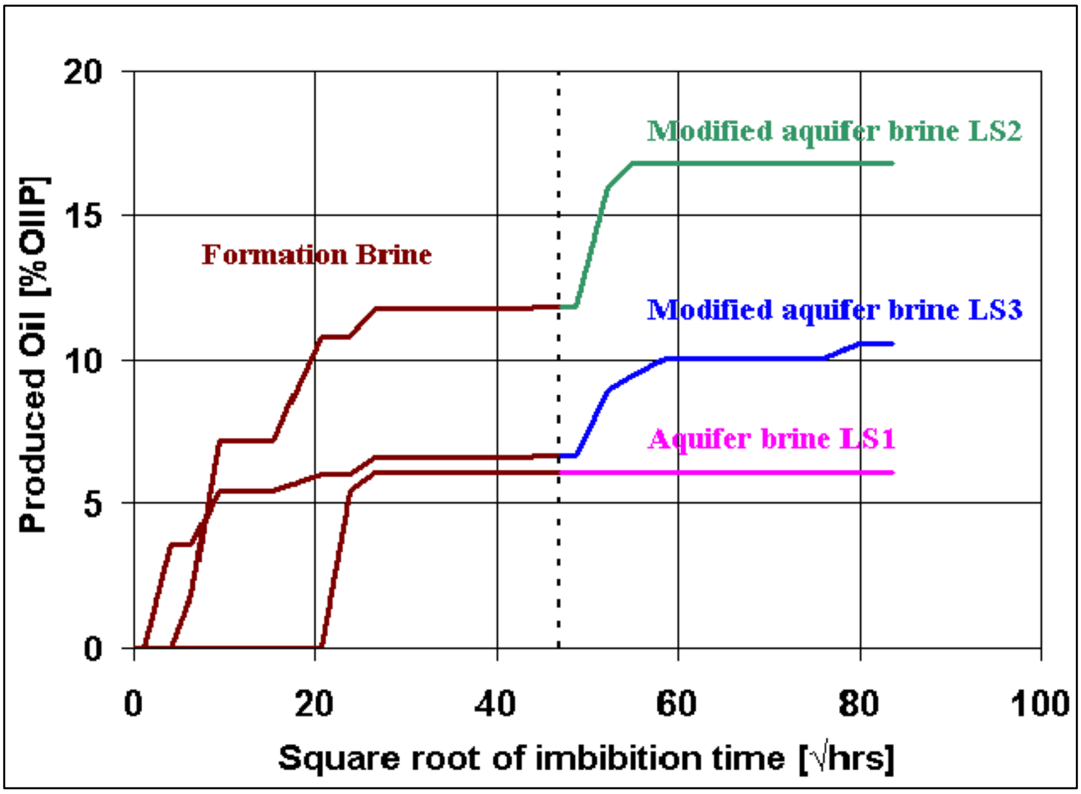


Figure 3. Results from spontaneous imbibition experiments on limestone core material at 60 ºC (Ligthelm et al., 2009)

Spontaneous imbibition tests` results reveal that a core sample surrounded by formation brine LS1 had no response in incremental oil recovery. The results are presented in Figure 3. The authors attributed this to the low content of sulfate or calcium ions (PDI). Whereas brines LS2 and LS3 resulted in oil production, an indication of wettability alteration towards more water-wet state and release of oil components. LS2 modified aquifer brine showed an incremental 10% OIIP, while LS3 recovered incremental 4% of OIIP. From these results, it can be concluded that it is possible to alter the initial wettability of the carbonate rock by manipulation of the ionic content of the injected brine. Excess of sulfate ions had a superior effect than lack of calcium ions because an extra 6% of OIIP can be recovered by LS2 brine. Moreover, during these SI experiments by LS2 and LS3 brines oil expulsion occurred during the first 30-hrs. After this time, there is no significant oil production. It can be concluded that calcium and sulfate ions increase the rate of wettability alteration. (Ligthelm, 2009)

At the same time, Yousef and his research group in 2010 aimed to study the impact of salinity and ion composition of the injected water to enhance oil recovery in carbonates at reservoir conditions and define the recovery mechanism behind this process by sequential injection of seawater in core flood experiments. For their laboratory measurements, they used different dilutions of synthetic seawater (twice diluted, 10 times, 20 times, and 100 times). Initially, seawater had a salinity of 57,600 ppm, while connate water that forms S_{wi} had 213,000 ppm, and the concentration of SO_4^{-2} and Mg^{+2} in synthesized seawater used in these experiments was two times more compared to typical seawater. These slugs of sea water were injected one after another in descending order of dilution, starting with seawater and ending with 100 times diluted seawater.

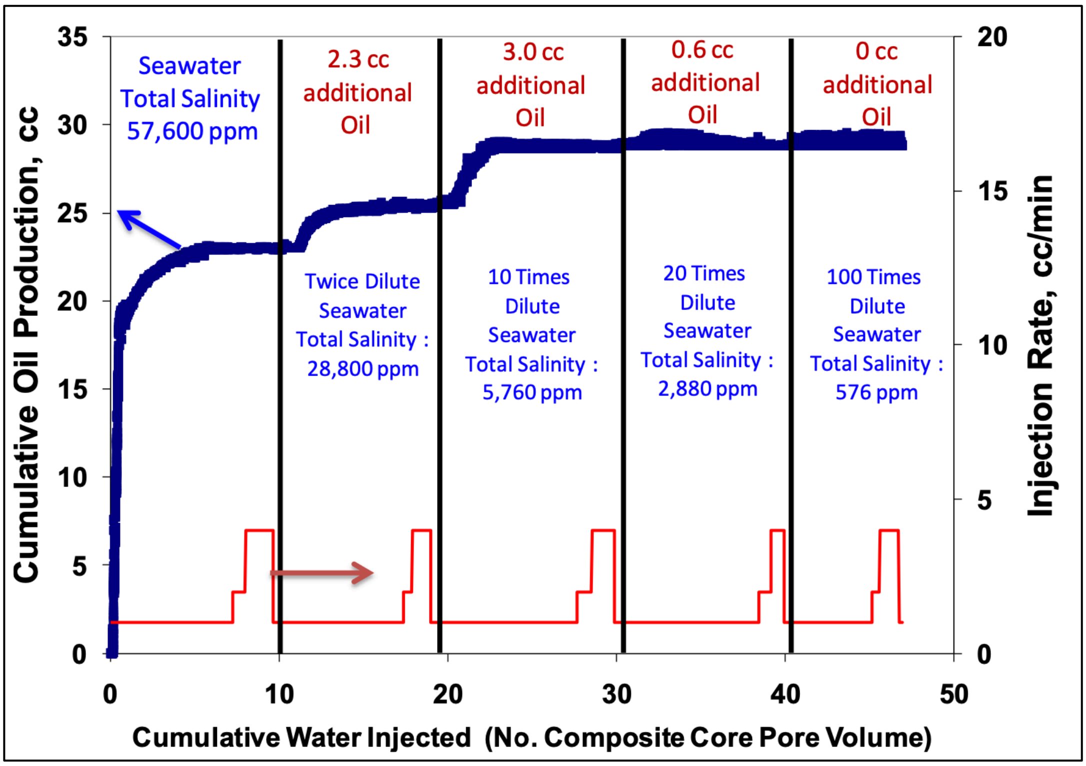


Figure 4. Cumulative oil production curve of the coreflood experiment. The blue curve represents the amount of oil produced through all injected salinity slugs of seawater, and the red curve represents the injection rate profile implemented during the coreflood experiment. (Yousef et al., 2010)

From core flooding results illustrated in Figure 4, the following conclusions can be made: it was possible to achieve 67% of OOIC with regular seawater (57,600 ppm), additional 7% of OOIP by 2 times diluted seawater (28,800 ppm), additional 10% of OOIP were recovered by 10 times diluted seawater (5,760 ppm), only 1.6% of incremental OOIP were recovered by 20 times dilutes seawater (2,880 ppm) and finally no additional oil was recovered by 100 times diluted seawater. (Yousef et al., 2010) Positive results of cumulative oil production demonstrated the positive effect of low salinity and its significant potential of "smart waterflooding" to be one of the EOR methods applied to carbonate reservoirs. Additionally, from the obtained results, it can be seen that there is an optimum salinity at which the highest incremental oil recovery exists. In this case, it is 10 times diluted seawater with an additional

10% of OOIP. Further dilution will have no significant effect on oil recovery. To determine the process which stands behind incremental oil recovery, IFT and contact angle measurements were performed by Yousef and his group. The pendant drop instrument was used for contact angle measurements. The results revealed that there is an insignificant IFT reduction due to salinity change. However, 2 times diluted seawater changed the contact angle from 90^0 (intermediate wet condition) to 80^0, 10 times diluted seawater was able to decrease it further up to 70^0, and no significant changes were observed with 20 times and 100 times diluted seawater. Wettability alteration was also confirmed by nuclear magnetic resonance (NMR) T2 distribution results conducted by Yousef and his research group. Finally, the substantial oil recovery observed during these core flood experiments is mainly due to wettability alteration, from intermediate wet to water-wet state caused by fluid-rock interactions.

In 2011 Gupta and his research group demonstrated the potential for AIM (Advanced Ion Management) trademark of ExxonMobil company for increased oil recovery by using different smart water with low salinity content compared to formation brine in tertiary mode waterflooding by conducting core flood experiments using dolomite and limestone cores. The idea of AIM is based on a calibration of water salinity and its composition by adding or removing certain ions. In their experiment, they used different types of brines: 1. Formation brine (FW), 2. Seawater (SW), 3. Seawater without sulfate (SW w/o SO_4^{-2}). Seawater with four times the usual sulfate concentration (SW with 4* SO_4^{-2}), 5. Formation water without calcium and magnesium ions (FW w/o Ca and Mg), 6. Formation water without calcium ions (FW w/o Ca). Tertiary mode waterflooding with SW with 4* SO_4^{-2} resulted in an additional 9% of OOIP after secondary flooding with formation brine that reached 61.6% of OOIP on dolomite cores. The same experiment was performed with limestone cores and resulted in an additional 5.1% of OOIP in tertiary mode and 55.8% of OOIP in secondary mode. However, due to anhydrite present in limestone cores, it was recommended to add extra. Another important aspect of this study lies in the performance of borate and phosphate ions and their superior effect on oil recovery compared to sulfate ions. In tertiary recovery mode, an additional 15.6% of OOIP was produced by using seawater containing borate salt. Sulfate ions were selectively removed to eliminate its contribution to any oil production. Figure 5 shows the trend of oil recovery vs PV of injected brine. Following the same experiment using seawater with phosphate ions, it was possible to recover an additional 21.3% of OOIP as shown in Figure 6. Generally, incremental oil recoveries reached by different smart waters are higher than those by using formation brine. By these results, it can be concluded that low salinity water has a high potential for enhanced oil recovery, and that presence of certain ions such as sulfate, borate, phosphate is essential for wettability alteration processes, the main cause for enhanced oil recovery. (Gupta et al., 2011)

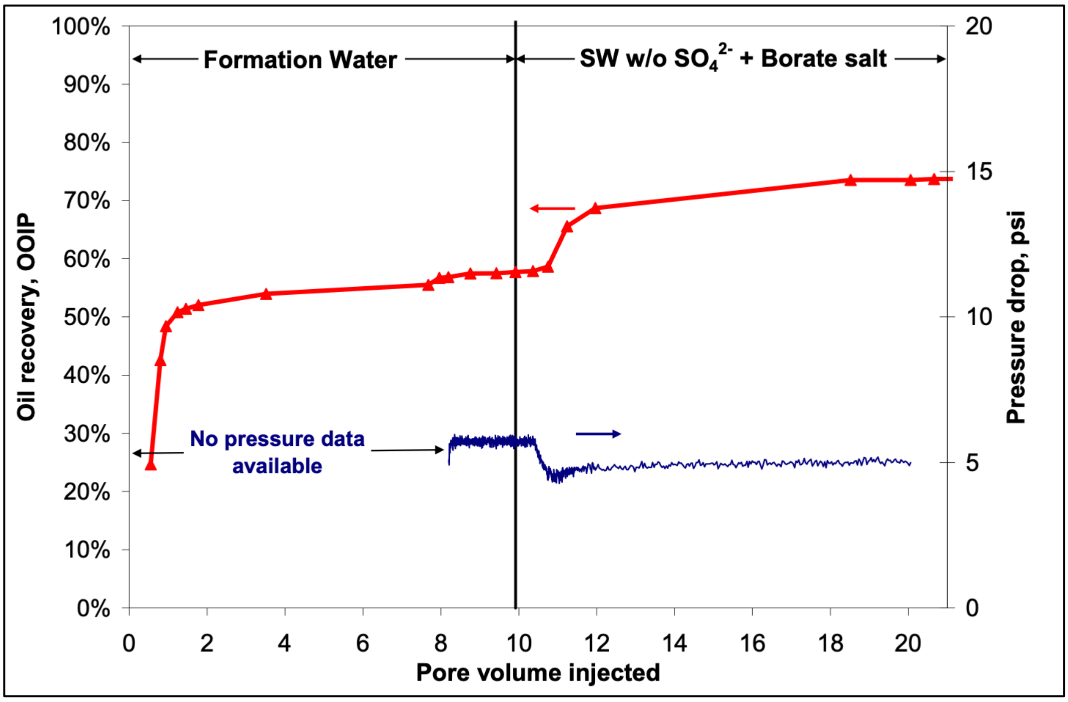


Figure 5. Oi recovery vs PV injected for brine containing borate salt under tertiary recovery. (Gupta et al., 2011)

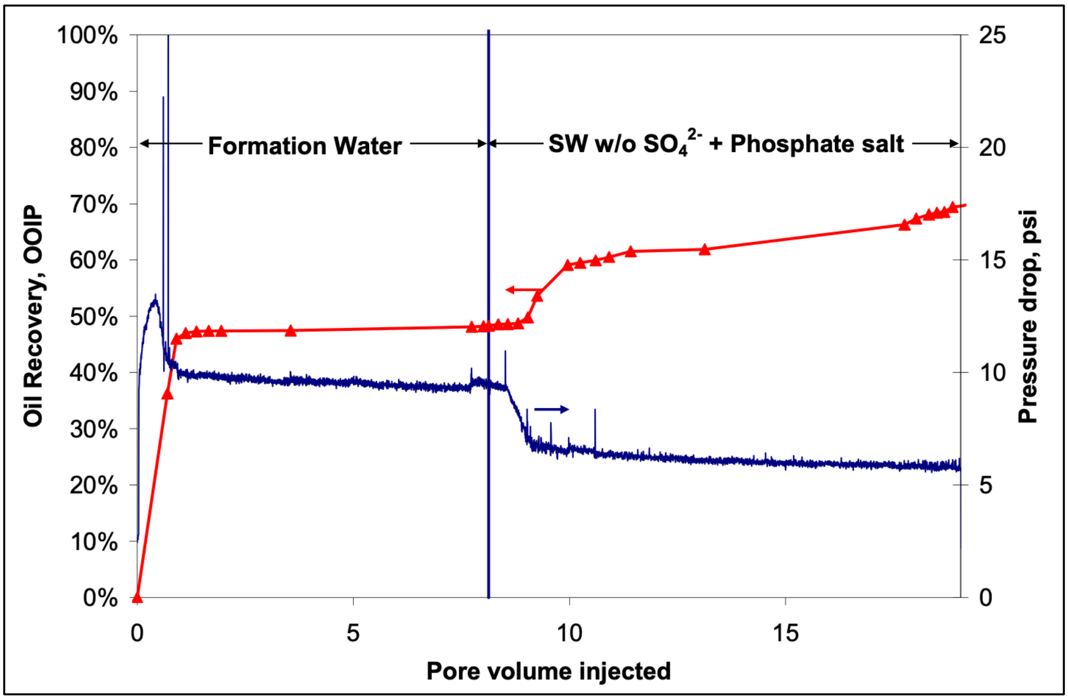


Figure 6. Oi recovery vs PV injected for brine containing phosphate salt under tertiary recovery. (Gupta et al., 2011)

All of the work described above is only a small part of the body of research conducted on LSW that proves its effectiveness in oil recovery processes. In the end, most researchers came to the same conclusions:

1. There are an optimum salinity concentration and certain composition of brine that could result in incremental oil recovery

2. Low salinity / smart waterflooding has positive results at the tertiary recovery processes

3. The main cause of low salinity/smart waterflooding is wettability alteration, and a change of wettability happens rapidly.

1.5 Problem definition and objectives of the thesis

Smart waterflooding is a new enhanced oil recovery method that has already shown positive results in laboratory and field scales. Extensive work was done to study the effect of dilution, the role of certain ions and other different parameters influencing its performance. However, there is a need to design an economical and effective scheme for smart water flooding on field scales, including estimations of required volume of brine to be injected, interaction times, flow rate, etc. Moreover, there are very few scientific works on the study of the Caspian Sea water and the Kazakhstan region. However, the Caspian Sea region contains a large volume of oil and natural gas from both offshore and onshore deposits and is considered as a strategic and important region. All large known oil fields of Kazakhstan are located in this region. Therefore, there is an urgent need for research and implementation of Caspian Sea water in smart water projects there, as this region is an important source of global energy. In addition, most previous projects were conducted at a tertiary recovery stage. Very little work was done to investigate the effect of smart waterflooding in a secondary recovery mode. Therefore, by this study, we aimed to investigate the role of different ions in Caspian Seawater on the rate of wettability alteration. To make such projects to be easily implemented and economical, we have addressed the following questions: How fast is the process of wettability alteration, and is it possible to produce incremental oil in a short time?

The main three objectives of this project are:

- To find an optimum brine composition based on dilution and ion composition change of Caspian Sea water for wettability alteration utilizing contact angle measurements.
- To investigate the underlying mechanism of smart waterflooding utilizing ion chromatography and pH analysis.
- To assess the rate of wettability alteration by spontaneous imbibition tests at reservoir conditions in secondary recovery mode.

1.5.1 Thesis structure

The thesis consists of five chapters: 1. Introduction, 2. Literature review, 3. Materials and Methodology, 4. Results and Discussion, 5. Conclusion and Recommendations. Global energy trends, oil need, an overview of oil recovery phases, and general insights into the history of low salinity waterflooding are presented in the Introduction. The driving mechanism of smart waterflooding and parameters affecting its performance are presented in the literature review. Materials and methodology part describe the step-by-step procedure of performed laboratory work. Then, the results are processed and analyzed in the Results and Discussion section. Finally, the key findings of the work together with future recommendations are presented in the last chapter of the thesis.

2 LITERATURE REVIEW

2.1 Wettability of the rock

Wettability is one of the essential parameters of the CBR system, which affects fluid distribution and ultimate recovery. It is defined as a tendency of one fluid to stick or adhere to the surface of the rock in the presence of other immiscible fluids. (Craig, 1971). Wettability is a property that refers to the interactions between the rock and fluids in the system. Depending on the affinity of one fluid to preferentially spread over the solid surface, it is classified an oil-wet, water-wet or intermediate system as shown in Figure 7 below.

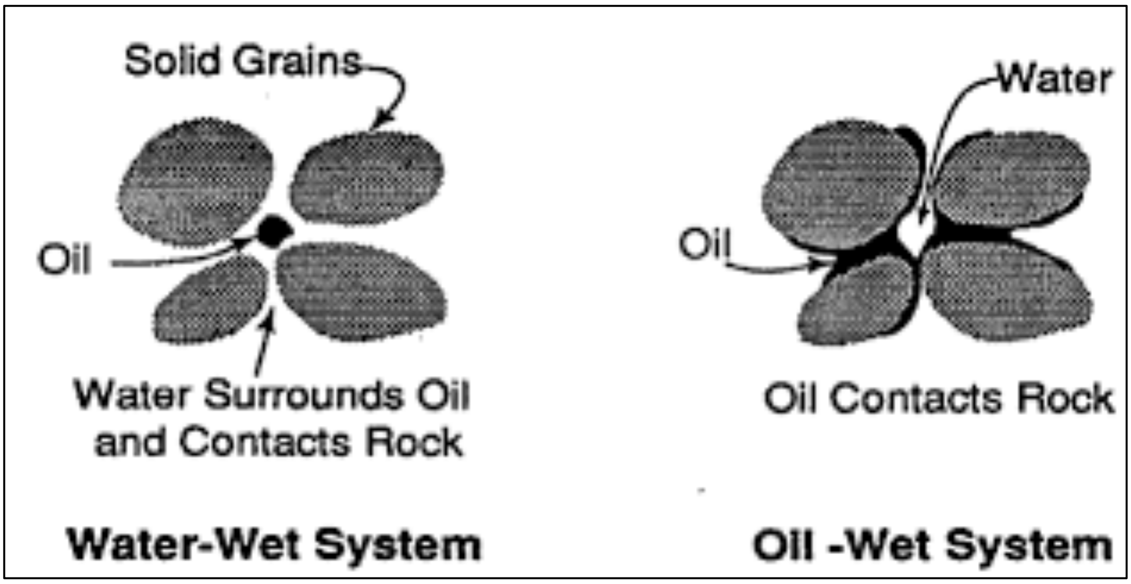


Figure 7. Water-wet vs Oil-wet systems. (Forrest F. Craig, 1971)

In a water-wet system, the rock surface is coated with a continuous layer of water resulting in the accumulation of oil in the center. So, water occupies small pores, while oil is in larger pores. Whereas, in an oil-wet system, oil has more affinity to stick to the rock surface, so it forms a continuous film around the rock surface. Wettability of the system can be measured through a contact angle of a denser fluid. If $\theta = [0^\circ - 30^\circ]$ this is a strongly water-wet system; if $\theta = [90^\circ - 110^\circ]$, the system is intermediate wet, and if $\theta = [150^\circ - 180^\circ]$, this is a strongly oil-wet system. Also, due to variations in mineralogy and surface chemistry, the rock can be water wet in one part but oil-wet in another part of the rock. This is known as a mixed wet system.

There are three main methods to determine the wettability of a CBR system, including 1. Contact angle measurement; 2. Amott test; and 3. US Bureau of Mines (USBM) method. During this study, we have utilized the contact angle measurement technique. This is a quantitative method that measures the angle between a rock surface and an oil drop in the presence of another fluid. Figure 8 illustrates the schematic of the contact angle measuring technique. In our lab experiments contact angle measurements were performed on a porous rock surface in a short time and until the equilibrium between phases was reached. As this were quick measurements, the effect of imbibition of a phase into the rock associated with wettability change into is negligible.

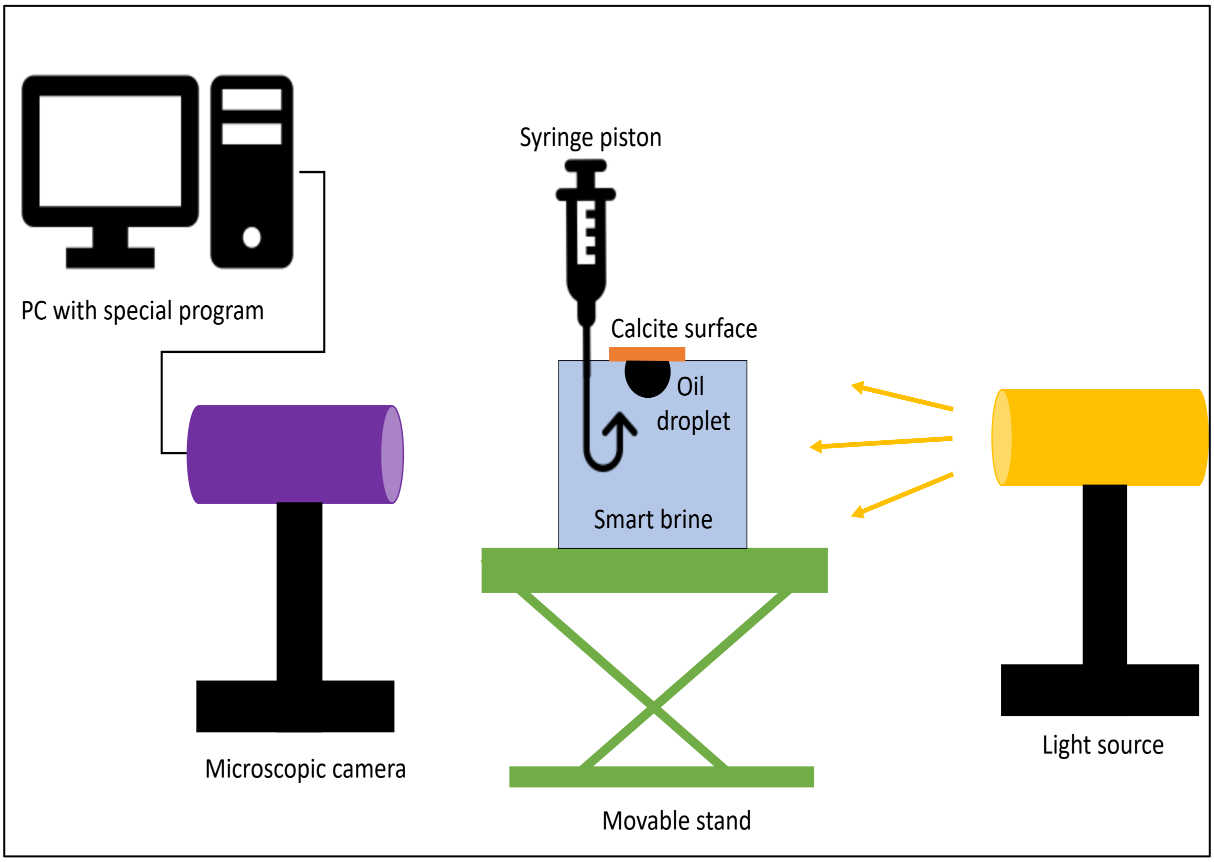


Figure 8. Schematic of contact angle measurement system

2.2 Driving mechanisms of low salinity water flooding in carbonates

To date, the suggested main mechanisms involved in low salinity/smart waterflood in carbonates include multi ion exchange (MIE) and rock dissolution. The objective of this section is to summarize and report the main findings of researchers on possible mechanisms behind low salinity effect in carbonate rocks. (Al-Shalabi, 2017); (RezaeiDoust, 2009).

2.2.1 Multi component Ionic Exchange (MIE)

All the components of the CBR system are in chemical and thermodynamic equilibrium. By introducing low salinity or smart water into the existing system, we change its equilibrium. It is well agreed and accepted by most researchers that wettability alteration is the main cause of oil recovery. This alteration can occur because of changes in surface potential by adsorption of some ions due to their higher affinity and desorption of organic material. In the multi-ion exchange (MIE) process, the role of sulfate ions as a catalyst for increasing rate in spontaneous imbibition tests was demonstrated by Strand et al. in 2003. The presence of sulfate ions turned the carbonates from intermediate/oil-wet to more water-wet state at different degrees, depending on the concentration content and carbonate rock types. (Strand, 2003)

Another valuable work that confirms the importance of SO_4^{-2} ions is done by Zhang and his research group in 2006. They also concluded on the significance of calcium and magnesium cations, and that simultaneous presence of sulfate with calcium or magnesium can change the initial rock wettability. They have conducted two tests at temperatures lower and higher than 100 ^{0}C and came to the following conclusions. There are two possible ways for the multi-ion exchange to happen: 1. At $T < 100$ ^{0}C, due to the high reactivity of sulfate ions, they are adsorbed on the carbonate rock surface, while negatively charged carboxylic material is desorbed. At the same time, the adsorption of calcium also increases, resulting in its excess near the surface. This excess of calcium reacts with oil components and takes some of the oil out to production; 2. At $T > 100$ ^{0}C, due to high activity of Mg^{+2} compared with Ca^{+2}, they replace calcium ions. (Zhang P., 2006) The schematic illustration of proposed mechanisms for wettability alteration in carbonates is illustrated in Figure 9 below.

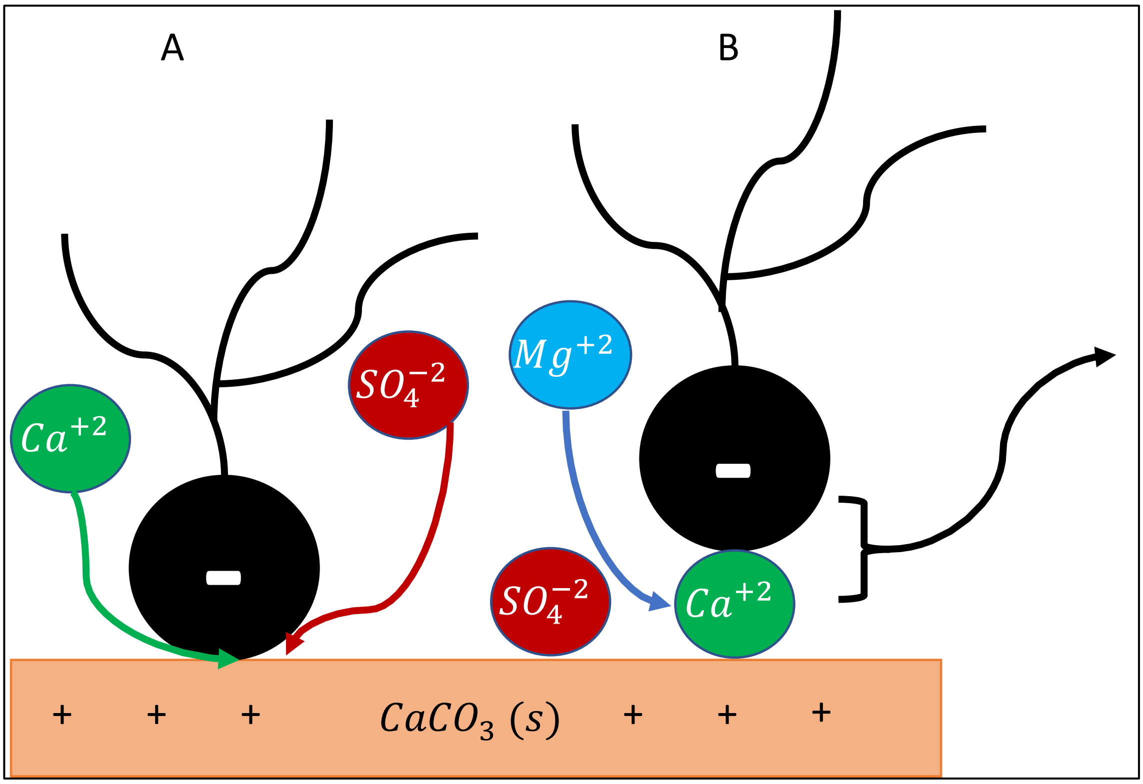


Figure 9. Proposed mechanism for wettability alteration in carbonates by (Zhang P., 2006)

2.2.2 Rock dissolution

Another suggested mechanism of incremental oil recovery is rock dissolution proposed by Hiorth et al. in 2010. They stated that the reasons behind oil displacement in core flooding experiments and spontaneous imbibition of water that produces oil might be different. Their chemical model clearly illustrated two possible mechanisms of changes in the CBR system: 1. Sulfate adsorption onto the carbonate rock surface due to its higher affinity; 2. Calcite mineral dissolution to establish a new equilibrium in the system. Carbonate mineral dissolution reaction is written below:

$$CaCO_3\ (s) + H_2CO_3(aq) \leftrightarrow Ca^{+2}(aq) + 2HCO_3^-(aq)$$

Moreover, it was shown that carbonate rock surface potential does not depend on changes in water chemistry and temperature, which makes it not a complete explanation of oil recovery in core flooding experiments. In their experimental work, they used pure carbonate rock samples and two types of water: formation and seawater and conducted experiments at different temperatures. Based on their results carbonate dissolution is suggested to be one of the controlling factors of incremental oil recovery. (Hiorth, 2010)

Shariatpanahi et al. in 2015 performed several experiments to understand the chemical mechanisms behind low salinity effect in limestone cores. They have found some anhydrite in their core samples, which appeared to be a key factor to observe low salinity effect. Their results reveal that once the brine salinity content is decreased by decreasing NaCl inactive salt concentration the dissolution of anhydrite increases. Anhydrite dissolution reaction is written below:

$$CaSO_4\ (anhydrite) \leftrightarrow Ca^{+2} + SO_4^{-2}$$

As a result, sulfate ions are generated in-situ and contribute to wettability alteration by ion exchange with the carbonate rock surface. With an increasing dilution ratio of water, sulfate generation is enhanced, resulting in higher oil recovery. Overall, it can be concluded that the presence of some anhydrite in carbonate cores has a positive effect on low salinity waterflooding. (Shariatpanahi, 2015)

2.3 Smart Water Slug Injection

Extensive research has been conducted on low salinity/smart waterflooding in carbonate rocks. Many laboratory experiments and several field trials verify the positive effect of low salinity and the importance of brine chemistry. [1-21] However, most of the research projects were dedicated to studying only the waterflooding process considering the drive mechanisms behind incremental oil recovery, the impact of concentration and ion composition, the effect of different parameters on fluid-fluid and fluid-rock interactions of the CBR system. No one addressed the problem of designing the process of waterflooding itself. To reach certain oil recovery in the field scale, the major problem lies in the preparation of a huge volume of injected brine with certain composition, which indeed is time-consuming and economically not practical. So, several researchers working in this field suggested a novel and more practical approach as Smart Water Slug (Shock) Injection (SWSI). The idea is to inject smart brine for a small amount of time and see the response of the system. Therefore, the objective of this section is to summarize different work done on this area of research and to assess the potential of SWSI as an EOR method for carbonate rocks.

Currently one of the Omani carbonate fields is under the waterflooding project, which utilizes base water (BW) for the injection. The main objective of Al-Kharusi B., et al. in 2018 involved in this research group is to improve the performance of base water to increase the incremental oil recovery of the field. Based on the positive results of low salinity/smart waterflooding and taking into account a problem of preparing a huge volume of water being used for continuous injection and economic feasibility of the project, they have proposed an idea of smart water slug injection (SWSI) of base water with an optimum concentration and ion composition for the tertiary recovery process. In their study, they used six different brines for core flooding: formation brine (FW with 136,200 ppm); base water (BW with 44,800 ppm); LS1 – 10 times diluted base water to study the effect of dilution; LS2 – 10 times diluted base water spiked with 4 times Mg^{+2} ions to study the effect of magnesium ions; LS3 –base water with 4 times SO_4^{-2} to study the effect of sulfate ions; LS4 – 10 times diluted base water spiked with 4 times Mg^{+2} and SO_4^{-2} to study the simultaneous effect of magnesium and sulfate ions. They have excluded the brine containing calcium ions because of precipitation and incompatibility with oil. In order to select an optimum brine composition, core plugs were placed into containers with different brines for two days at 87 ^{0}C. From contact angle measurements` results, the highest change occurred in LS4 brine, from original 90^0 (intermediate wet when flooded with BW) to 0^0 (completely water wet). In addition, Zeta potential measurements confirmed that LS4 is an optimum brine as it significantly changed the surface charge of the carbonate rock. Initially, it was -29.9 mV and after treatment of the core in LS4, it became -15.5 mV. After the selection of an optimum brine which is LS4, a slug with a size of 0.5 PV containing selected brine was injected into the core and followed by injection of formation water. As a result, by the slug injection of an optimum brine, it was possible to recover an additional 4.3% of OOIP as depicted in Figure 10. Based on diagnostic tests the proposed mechanism behind tertiary oil recovery was the multi-ion exchange between sulfate, magnesium, and calcium ions and adsorbed organic ions at the surface of the carbonate rock and rock dissolution. (Al-Kharusi, 2018)

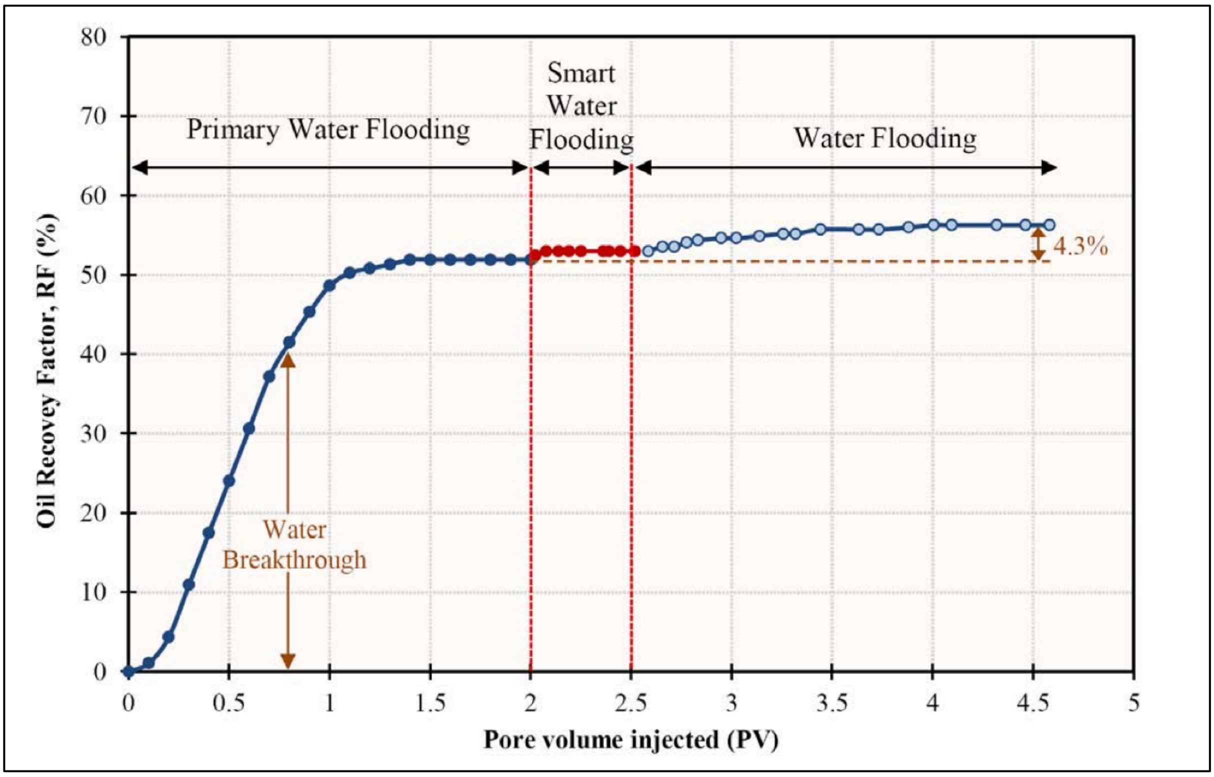


Figure 10. Oil recovery vs PV injected of smart brine (Al-Kharusi et al., 2018)

This research work shows the importance of low salinity effect and potential determining ions: the presence of sulfate, magnesium or calcium ions is essential for wettability alteration process, it was proved that sulfate has a higher positive effect on oil recovery, but its simultaneous presence with magnesium ions can further improve the recovery process. In addition, even a short interaction time with smart water can recover a substantial amount of incremental oil. In general, positive results of core flood experiments reveal that SWSI is an economical and more practical design of smart waterflooding that can be applied for enhancement of oil recovery. Finally, to quantify the economic benefits of such projects, it is recommended to perform an economical study of the above research work and compare the results with usual smart waterflooding that yield the same oil recovery in tertiary mode.

All experimental results obtained in the previous research work clearly demonstrate the potential of smart water slug injection using carbonate core samples. Another group of researchers including M. Fani, H. et al. (2018) also have conducted several experiments on optimization of smart water flooding in carbonate reservoirs. The aim of their work was to verify that even small slugs of smart water can recover additional oil as affectively as larger sizes of smart water. Previously, extended research has been performed on the effect of salinity content and ion composition of the injected brine. Hence, it was proved that incremental oil recovery is mainly controlled by divalent ions including Mg^{+2}, Ca^{+2}, SO_4^{-2} - (Shariatpanahi, 2015). Moreover, Al-Kharusi and her research group illustrated that the highest incremental oil recovery can be obtained when diluted base water with low salinity content spiked with sulfate and magnesium ions simultaneously - (Al-Kharusi, 2018). Therefore, M. Fani and his colleagues in their core flooding experiments used 2.65 g/mL of $MgSO_4*7H_2O$ as an injection brine in a tertiary mode at the same constant injection rate but with various slug sizes, such as 0.75, 1, 1.5, 2 PVs, followed by continuous injection of high salinity water. Production rates at the end of each stage, as well as pH and contact angle measurements, were recorded during the experiments. For the wettability alteration process, some time is required, so the flooding with small slugs of smart water was hindered for 12 hours. The production data they took during smart water flooding clearly showed that increasing the pore volume of the slug increases the incremental oil recovery. The reason behind this is that more volume of smart water can react with the CBR system. Although, the interaction time and contacted volume are important the production data taken during high salinity water flooding at the final stage of the experiment proved that even 0.5 PV can be as much effective as larger pore volumes of smart water as presented in Figure 11.

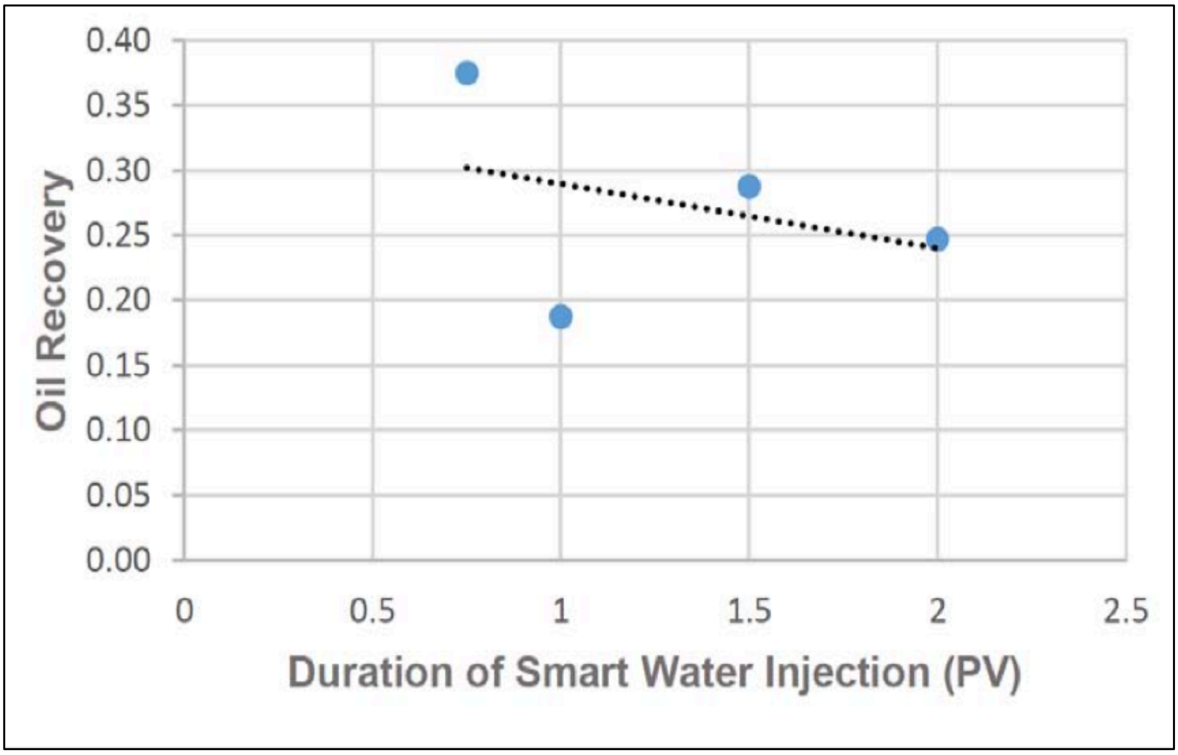


Figure 11. Oil recovery vs PV injected after high salinity flooding

Contact angle measurements and pH values recorded during the experiment verify the wettability alteration process by smart water - (Fani et al, 2018). The positive results of the Fani`s work again depict the fact that injection of even small slugs of smart water or smart water slug injection (SWSI) has a significant potential to improve oil recovery performance at tertiary mode, at the same time being a cost-effective and more practical design of smart waterflooding compared to traditional one.

In the previous two works, smart water was injected in the tertiary mode after the usual waterflooding process. In this study, we offer a new method to improve the performance of smart waterflooding. In order to optimize the process and reduce the volumes of high salinity brine, we were aimed to prove that a small interaction time with smart brine in a secondary mode, just after aging in crude oil could result in noticeable oil production by spontaneous imbibition tests.

3. Project schedule

The aim of this chapter is to provide a project Gantt chart and describe possible hazards and measures to control them during the project implementation. The project Gannt Chart is presented in Figure 12. It was developed to ensure that the project will be delivered on time.

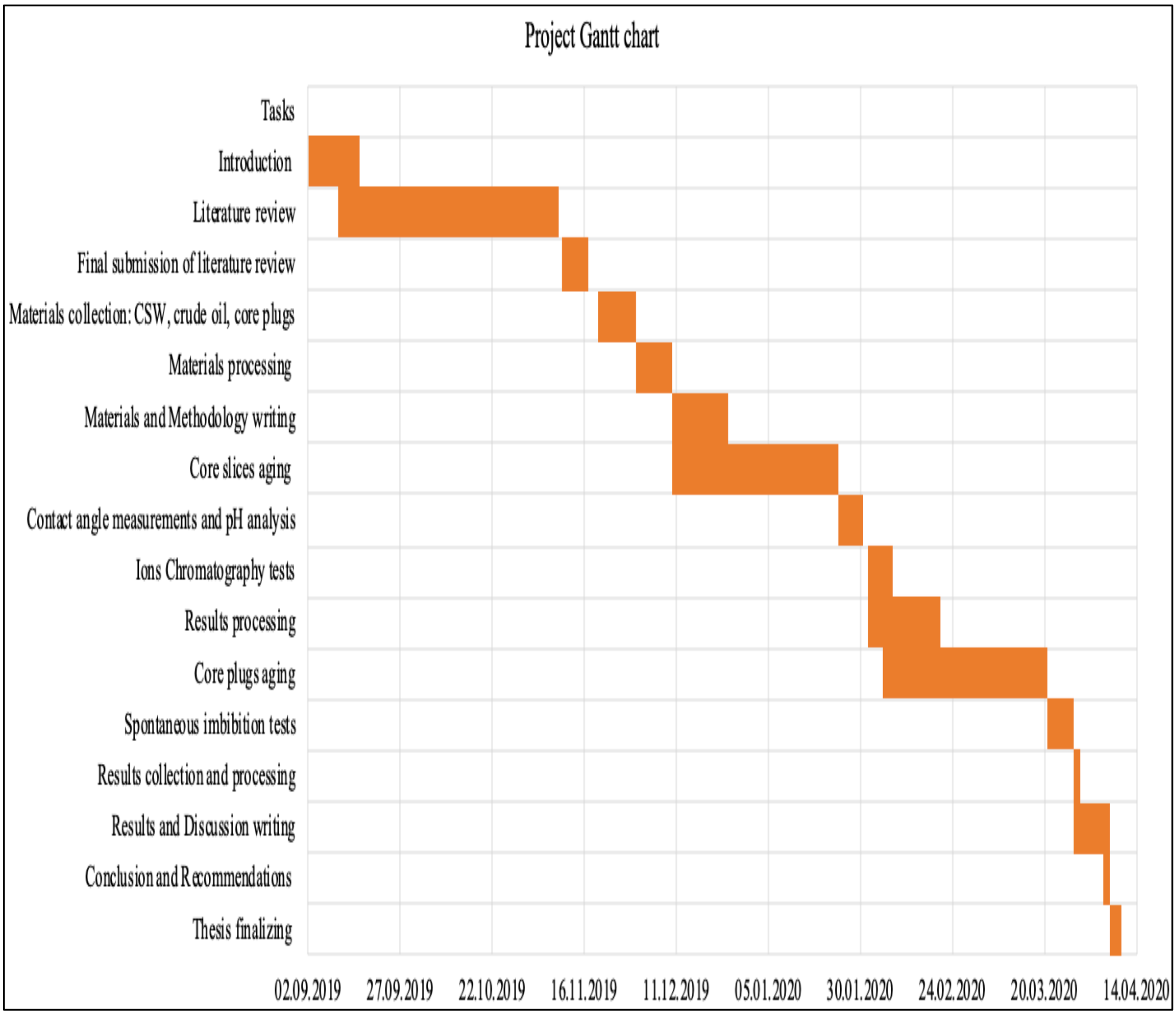


Figure 12. Thesis schedule

3.1 Resource requirements

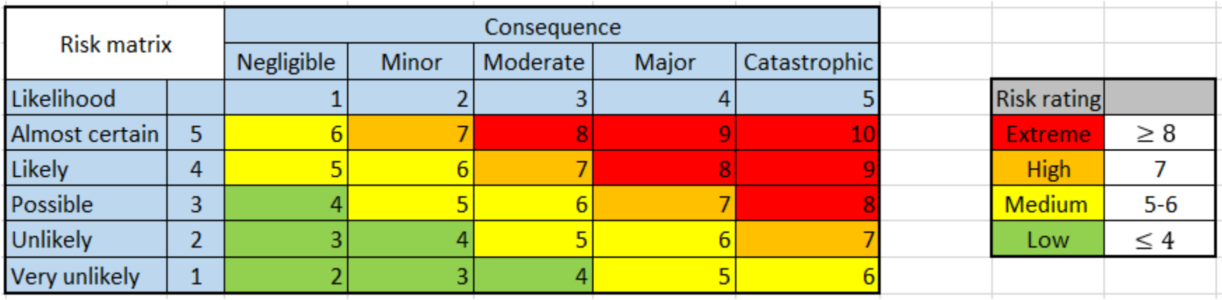
The necessary resources for project completion were identified and listed.

Table 1. Resource requirements

Device/material	Function
Laptop or PC	My own laptop or PC from computer lab is used to conduct the research
Caspian Sea water, crude oil, different salts, Indiana limestone core samples	To perform laboratory experiments
Contact angle measuring instrument, pH meter, Ion chromatographer, core aging cell, lab oven, Amott cells	To perform laboratory experiments
Printer	To print out articles or papers
Access to internet	To download essential materials related to my thesis

3.2 Risk management

Risk is a measure of probability of not achieving expected outcome, and it can be avoided or mitigated through proper planning. Risk mitigation plan was developed for this thesis to identify the possible risks and the ways of avoiding or controlling them. One of the common risk assessment tools is WRAC analysis that uses a 5x5 likelihood-consequence matrix. Table 1 illustrates the risk rating from low to extreme cases. Risk ranking matrix



Risk matrix		Consequence				
		Negligible	Minor	Moderate	Major	Catastrophic
Likelihood		1	2	3	4	5
Almost certain	5	6	7	8	9	10
Likely	4	5	6	7	8	9
Possible	3	4	5	6	7	8
Unlikely	2	3	4	5	6	7
Very unlikely	1	2	3	4	5	6

Risk rating	
Extreme	≥ 8
High	7
Medium	5-6
Low	≤ 4

Figure 13. Risk ranking matrix

3.2.1 Physical hazards

Physical hazard is a factor that can harm a person's mental or physical condition without the need for physical contact. The possible physical hazards that can occur during the thesis work and the ways to avoiding them are given in Table 2.

Table 2. Hazard description and risk control

Hazard type	Description	Risk rating	Risk Control
Physical	High pressure High temperature equipment	7 High	Lab coat, goggles, special gloves for high temperature
Chemical	Crude oil, salts, n-heptane: inhalation, corrosive, eye irrigation	7 High	Lab coat, googles, gloves

3.2.2 Project hazard

Project hazards are the factors that can affect to the provision of the thesis on time due to unexpected situations.

Table 3. Project hazards

Project hazard	Description	Risk level / rating	Risk control
Sudden computer crash	Accidental fall to the floor	3 Low	Obligatory carrying in a bag
Thesis related documents loss	Sudden failure of the hard drive, computer crash due to viruses, not saving the thesis files	5 Medium	Use cloud services like google drive, do not forget to save, installation of anti-virus software
Laboratory problems: lack of material, fail of equipment	Lack or not availability of material/samples to conduct the experiments; equipment may not work and require time for repair	7 High	To construct and follow working plan in such situations

4. Materials and Methodology

4.1 Core slices

Core slices employed for contact angle measurements were cut from Indiana carbonate outcrops with permeability on average of 180 mD. X-Ray Diffraction (XRD) analysis was made using Rigaku SmartLab Automated multipurpose X-ray diffractometer. XRD analysis illustrated in Figure 14 was matched with $CaCO_3$, the same peaks reveal that samples were dominantly made of calcite.

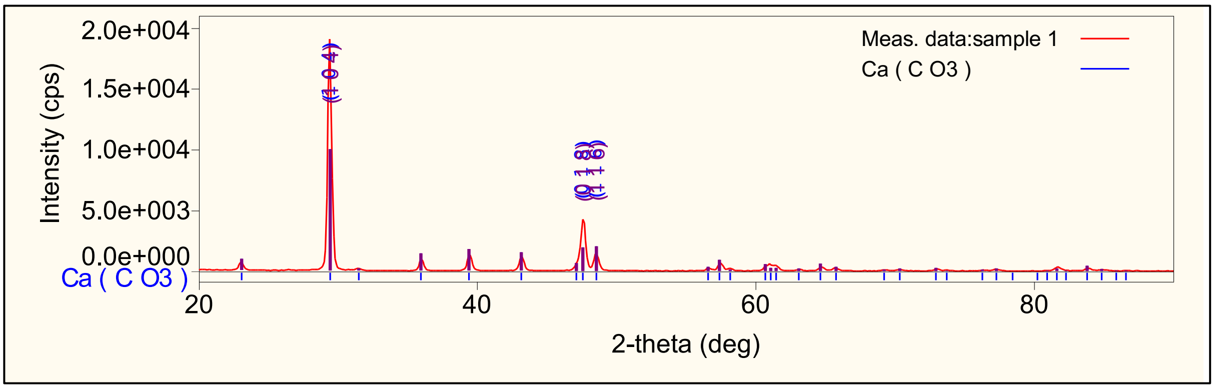


Figure 14. XRD analysis

Core slices had a semicircle shape with a radius of 4 – 5 cm and height of 1 cm as illustrated in Figure 15.

Figure 15. Core disks used in CA measurements

4.2 Crude oil

The oil is a dead oil from one of the fields in the west region of Kazakhstan. The oil is taken from the field after the first filtration step, being separated from water and any mechanical impurities. The viscosity and density of the oil were measured using Anton Paar's viscometer at different temperatures, the results are presented in Table 4.

Table 4. Measured oil properties at different temperatures

Temperature [^{o}C]	20	50	80
Density [g/cm^3]	0.906	0.887	0.868
Viscosity [cP]	171.83	32.28	10.57

The composition of the crude oil was measured by utilizing Gas chromatography–mass spectrometry method, results are presented in Table 5.

Table 5. Crude oil composition

Component	Weight Percentage (%)
C_5	0.80
C_6	0.43
C_7	1.63
C_8	7.36
C_9	8.70
C_{10}	17.87
C_{11}	5.09
C_{12}	5.44
C_{13}	8.30
C_{14}	6.50
C_{15}	30.55
Other	7.66

4.3 Brines

High salinity formation brine was prepared based on the chemical composition of water from the Tengiz field to represent fields in west Kazakhstan in the Caspian Sea region. Water from the actual Caspian Sea was employed as a low salinity brine. Ion composition analysis of Caspian Sea water was done using Metrohm 930 Compact IC Flex - Ion Chromatographer. Low salinity brines were prepared by diluting Caspian Seawater, and smart brines were prepared by adding different salts into 5 times diluted Caspian Seawater. Ion concentrations were calculated based on chemical formula stoichiometry and molecular mass of compounds. Dilutions were made using deionized water. Tables 6, 7 represent the composition of all brines used during the experiment and the amount of added salt.

Table 6. Brines composition used to study dilution effect

	Formation brine	Caspian Sea Water	5X_dilution	10X_dilution	20X_dilution	Deionized water
ANIONS						
Chloride	104980	7215	1443	722	361	0
Sulfate	-	3145	629	315	158	0
CATIONS						
Sodium	54500	4975	995	498	249	0
Potassium	-	155	31	16	8	0
Calcium	9450	535	107	54	27	0
Magnesium	1450	770	154	77	39	0
TDS [ppm]	170400	16795	3359	1682	842	0

Table 7. Brines composition used to study ions effect

	5X	5X_Mg	5X_Ca	5X_SO4	5X_Mg_SO4	5X_Ca_SO4
Additive salt [g/L]	-	$MgCl_2*6H_2O$ 4.72	$CaCl_2$ 1.88	Na_2SO_4 2.03	$MgSO_4$ 2.14	$CaSO_4*2H_2O$ 2.51
ANIONS						
Chloride	1443	3134	2660	1443	1443	1443
Sulfate	629	629	629	2003	2270	2061
CATIONS						
Sodium	995	995	995	1726	995	995
Potassium	31	31	31	31	31	31
Calcium	107	107	783	107	107	690
Magnesium	154	718	154	154	586	154
TDS [ppm]	3359	5050	5252	5464	5432	5374

4.4 Core slices preparation

Core slices were cut from Indiana carbonate outcrop and polished to have a smooth surface. Then all of them were saturated with formation brine at 80 °C for 2 hours in the laboratory oven to set up initial fluid distribution. Then, they were put into oil at 80 °C for 6 weeks in the laboratory oven to establish reservoir initial wettability conditions. Figures 16, 17 illustrate the aging process in the formation brine and crude oil.

Figure 16. Aging core samples by formation brines

Figure 17. Aging core samples by oil

4.5 Contact Angle Measurements and pH Analysis

After aging in oil, the slices were cleaned with a paper to remove an excess of oil from the surface. Finally, plates were soaked in different brine solutions at 80 ^{o}C for different time intervals: 3,6,9, 24, 48 hrs. Dynamic contact angle measurements were measured using the OCA 15EC video-based optical contact angle measuring instrument shown in Figure 18. All aging procedures and laboratory experiments were performed at 80 ^{o}C, as this is an average temperature of reservoirs located in the Caspian Sea region (Akhmedzhanov et al., 2012).

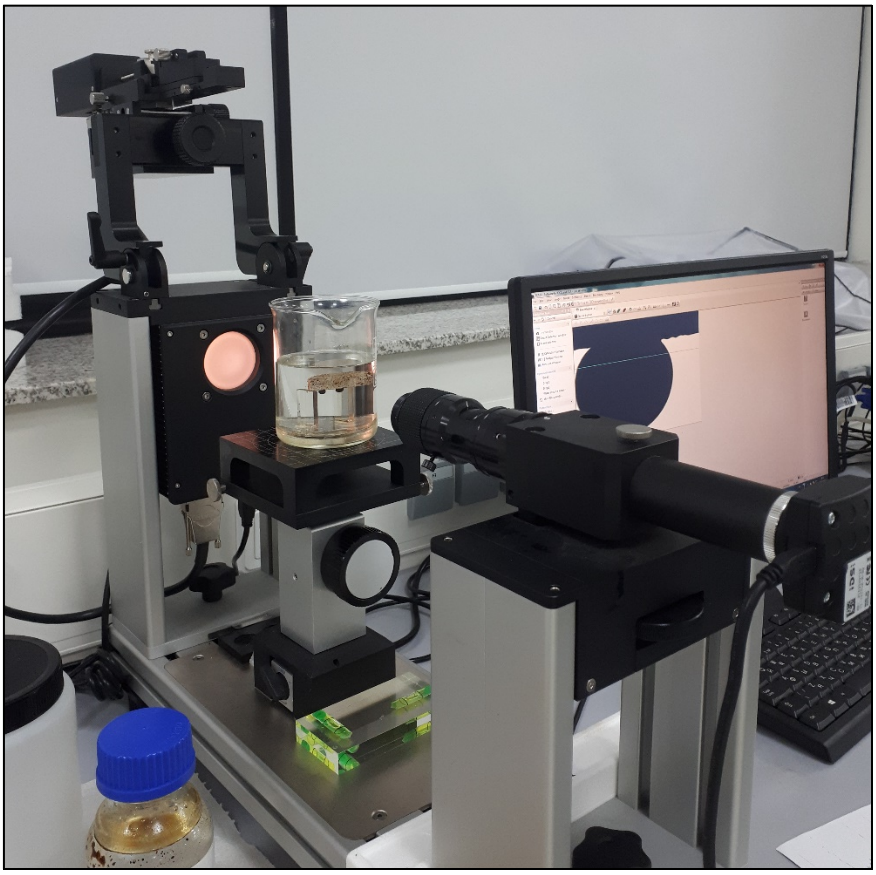


Figure 18. OCA 15EC video-based optical contact angle measuring instrument

Contact angle measurements were used to observe wettability alteration by different smart solutions. An angle between an oil drop and a rock surface was captured by taking a photo and analyzing it in SCA software version 4.5.14 Build 1064. The angle was measured by defining a baseline at the solid interface and drawing the tangent line to the oil drop contour. The instrument measures the left and right-side readings of the droplet. All the measurements were done three times, and the average value was reported in the Results section. The pH of the aqueous solutions before and after each surface treatment was also measured using pH mete

4.6 Ion Chromatography analysis

The ion chromatography instrument (Metrohm 930 Compact IC Flex - Ion Chromatographer) illustrated in Figure 19 was utilized to identify the ion composition of brines. Measurements were taken at the same time intervals as contact angle experiments. The maximum allowed salinity the equipment can tolerate is 4000 ppm. For this reason, all brines were diluted 100 times with deionized water.

Figure 19. Metrohm 930 Compact IC Flex - Ion Chromatographer

4.7 Core plugs preparation

The same Indiana limestone core plugs were used for spontaneous imbibition tests. They were cut in a 3-inch length as illustrated in Figure 20.

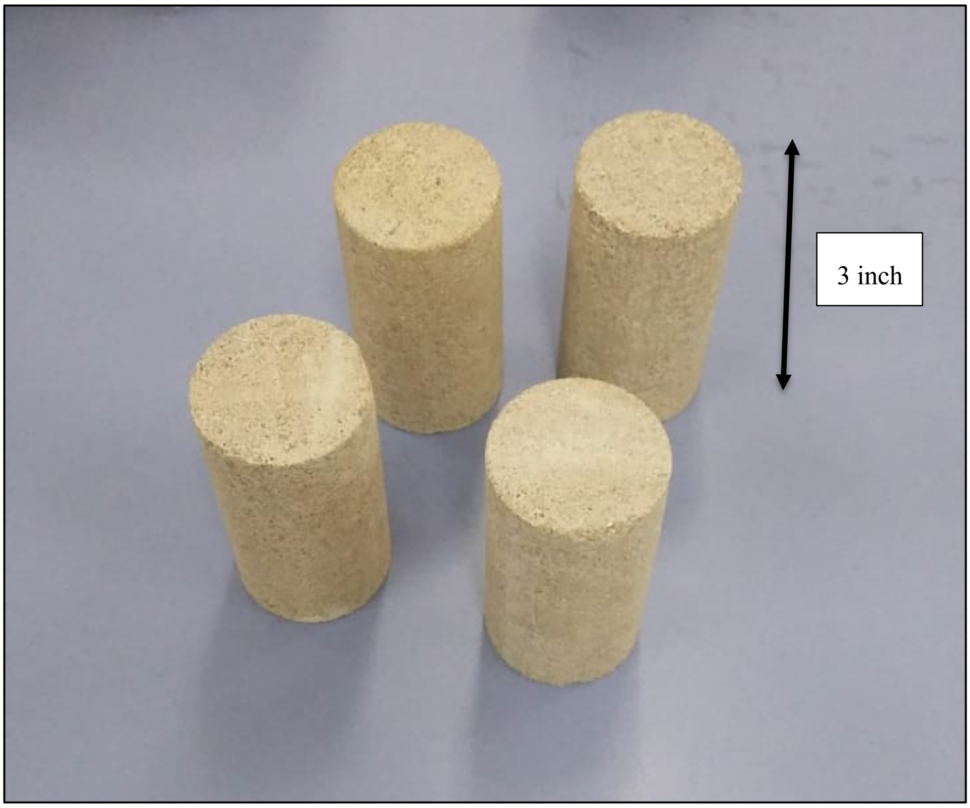


Figure 20. Indiana core plugs

The porosity was measured by Helium porosimeter as depicted in Figure 21. The cores were then saturated with formation brine under 1800 psi pressure for 1.5 days to establish initial wetting conditions. The porosity was rechecked by dry/wet weight method using the following formulas. Density of formation brine is equal to 1.1243 g/cc.

Equation 1. Formula to find porosity by dry/wet weight method

$$\phi = \frac{m_{wet} - m_{dry} / \rho_{FW}}{V_{bulk}}$$

Absolute permeability of cores was then calculated according to Darcy law by continuous injection of formation brine at different flow rates. At each rate, the pressure drop across the core was recorded. This was also done to make sure that the core was fully saturated with brine.

Equation 2. Darcy law

$$q = \frac{k * A * \Delta P}{\mu * L}$$

Then, the cores were flooded with crude oil at different flow rates in coreflood equipment as illustrated in Figure 22 until irreducible water saturation (S_{wi}) was reached. Finally, saturated cores were placed into oven for 6 weeks at 80 °C for aging procedure.

Figure 21. Helium gas Porosimeter by VINCI Technologies

All measured parameters and data are presented in Table 8. Dead volume of the tubes during flooding was measured to be $V_{dead} = 0.8$ ml. Irreducible water saturation was calculated according the following formula:

Equation 3. Formula to calculate irreducible water saturation Swi

$$S_{wi} = \frac{V_p - (V_{prod_{water}} - V_{dead})}{V_p}$$

Figure 22. Coreflood equipment

Table 8. Core plugs properties

Parameter	Core-1	Core-2
Length [mm]	75.58	75.77
Dry mass, m_{dry} [g]	185.75	192.01
Wet mass, m_{wet} [g]	204.85	207.63
Porosity, ϕ_1 (by gas)	17.19	16.93
Porosity, ϕ_2 (by water)	16.99	16.16
Pore volume, V_p [ml]	14.798	14.699
Produced water volume, V_{prod_water} [ml]	12.7 ± 0.2	12 ± 0.2
Absolute permeability, k_{abs} [mD]	47	19
Irreducible water saturation, S_{wi}	$19.6 \pm 1.4\%$	$23.8 \pm 1.4\%$
Initial oil saturation, S_{oi}	$80.4 \pm 1.4\%$	$76.2 \pm 1.4\%$
Relative oil permeability, k_{ro} [mD]	0.72	0.53

4.8 Spontaneous imbibition

Spontaneous imbibition experiments are carried out to test the potential change of rock wettability by introducing ion-engineered water. Spontaneous imbibition refers to the process of absorption of the phase into the rock without any pressure. An imbibition test is a comparison of the imbibition potential of water and oil into a rock. In this study, imbibition tests were performed as a secondary recovery process. For this purpose, two aged carbonate core plugs were placed into two separate Amott cells from VINCI Technologies and then placed in an oven at 80 ^{o}C for spontaneous imbibition tests. Schematic and laboratory photos of spontaneous imbibition tests are illustrated in Figures 23, 24 below. As was confirmed by contact angle measurements to be the most optimum brine for wettability alteration, 5X_Ca_SO4 was chosen to be the 1st imbibing fluid. And 2nd imbibition test was carried out by actual Caspian Seawater. For the reason that Caspian Seawater also showed promising results in CA alteration, and it was used as a base during all other brines preparation. A core plug with a permeability of 47 mD was used for imbibition test with Caspian Seawater, and a core plug of 19 mD was used with 5X_Ca_SO4 brine respectively. The differences in permeability of the cores affect the duration of imbibition. In a core with higher permeability, the number of small pores is less, as a result, the oil production may occur quicker. To eliminate such errors, a core with higher permeability was used with Caspian Seawater, and a core with lower permeability was used with an optimum brine. However, the difference in permeability of two cores is not significant. Therefore, the results of imbibition tests are comparable. The amount of produced oil was daily recorded. The oil recovery factor was calculated as a percentage of OOIP.

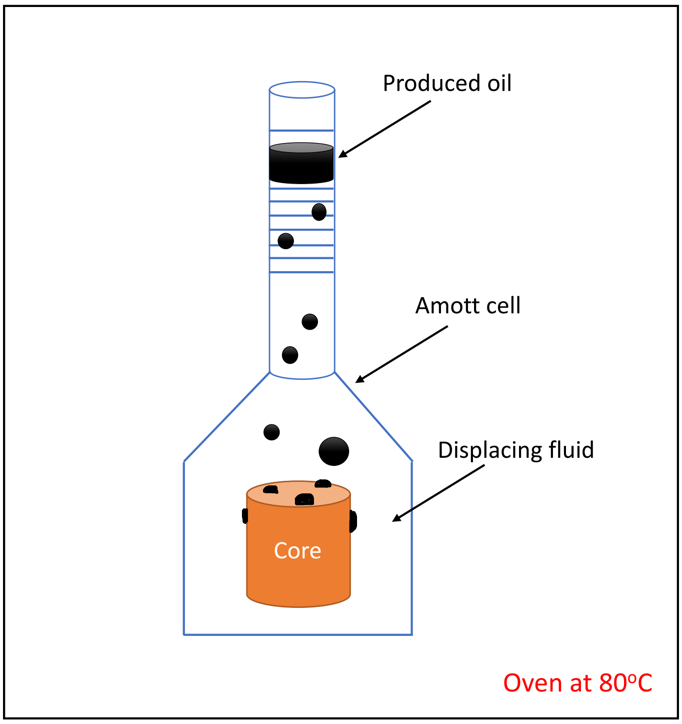


Figure 23. Amott cell schematic

Figure 24. Spontaneous imbibition test in the lab

5. RESULTS AND DISCUSSION

This chapter illustrates the results of the contact angle (CA) measurements, pH analysis, ion chromatography, and spontaneous imbibition test to show the effect of different ions on the wettability alteration rate of calcite surface. All experiments testing the effect of smart water were performed in a secondary recovery mode, immediately after aging in crude oil. The contact angle method was utilized as it is considered to be a useful method to easily visualize and detect wettability behavior. The underlying mechanism was investigated by conducting ion chromatography experiments of brine before and after each surface treatment. The CA was measured at ambient condition (25 ^{o}C and 1 atm) between three phases, an oil droplet, a rock surface, and the examined brine. At this temperature, the oil viscosity is higher compared to the oil viscosity at reservoir conditions. But, the effect of viscosity on static angle measurement is negligible. The average initial contact angle of the core slices before starting the inspection was 86^{o}, indicating the neutral wetting state. The following sub-sections present the finding of CA measurements.

5.1 Effect of dilution on contact angle measurements

The purpose of studying the effect of dilution was to identify the best dilution ratio of Caspian Sea water that could alter an initial wetting state of samples as much as possible. After 1.5-month of aging in crude oil, our samples reached the neutral wetting state. Then, they were divided into five groups and placed in five different brines, including deionized water, Caspian Seawater (CSW), 20 times diluted CSW, 10 times diluted CSW, and 5 times diluted CSW. The contact angle of an oil drop was measured after 3, 6, 9, 27, and 48-hrs. Figure 25 shows the progress of the wettability alteration of a carbonate rock surface by five tested brines. The provided photos below in Figure 26-30 also clearly demonstrate how the wettability of the rock changes to the more water-wet state while being aging in Caspian Seawater.

Several trends can be highlighted from this Figure 25. Firstly, it can be noticed that deionized water did not result in noticeable angle change and cannot be applied as a displacing fluid. This is in agreement with the work done by Ayirala (2019). As they stated, deionized water does not contain any active ions that could initiate rock surface`s wettability alteration. On the other hand, being immersed in a Caspian Sea water, 10 times diluted, and 5 times diluted brines, wettability alteration process initiated during the first 3-hrs of the interaction. Whereas, it took 9-hrs in case of 20 times diluted CSW. The reason for this observation can be possibly correlated with the minimum required concentration of potential determining ions (PDI) necessary to activate the wettability change process. Therefore, it can be concluded that to have an immediate response of the system to injection low salinity water the minimum salt concentration should be more than 850 ppm, the salt concentration of 20 times diluted CSW. Secondly, introducing the Caspian Sea water into the CBR system has shown significant results. It was able to shift the initial contact angle from 86° to 41° in two days. Moreover, dilution of CSW 5 times and 10 times has further decreased the angle up to 34° in two days. 20 times diluted CSW was also able to alter the initial wettability of the carbonate rock surface but only to 51°. Thus, there is an optimum dilution ratio and ion concentration which could result in optimum contact angle alteration. For this reason, to see this trend a graph of contact angle change and ions concentration was plotted in Figure 31 for all time intervals.

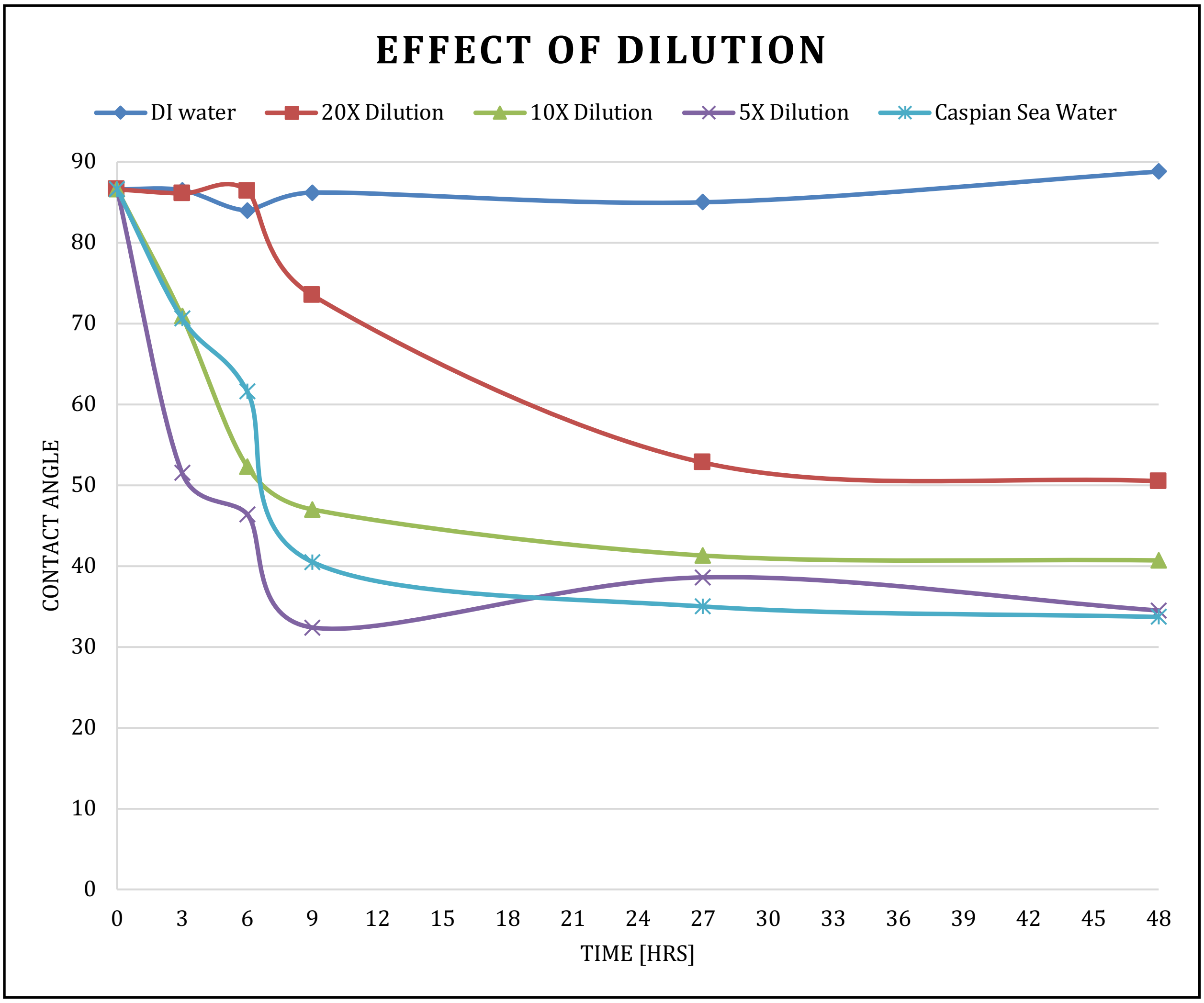


Figure 25. Effect of dilution on CA measurements

Figure 26. After aging in Caspian Sea water for 3-hrs

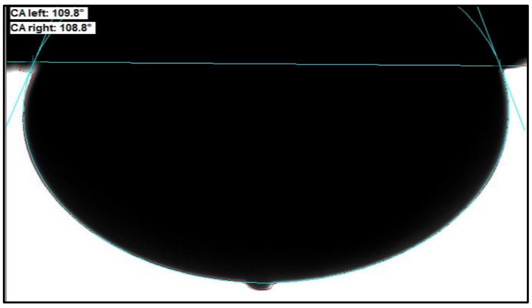


Figure 27. After aging in Caspian Sea water for 6-hrs

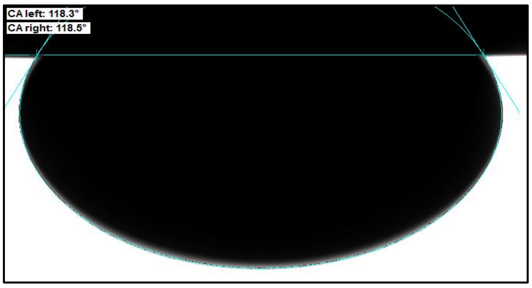


Figure 28. After aging in Caspian Sea water for 9-hrs

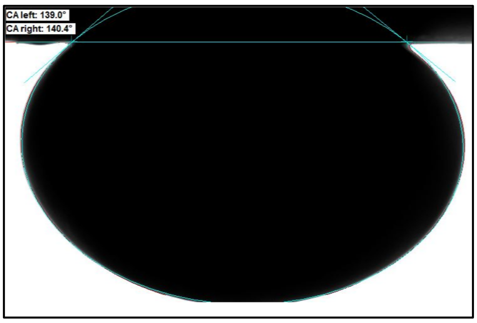


Figure 29. After aging in Caspian Sea water for 27-hrs

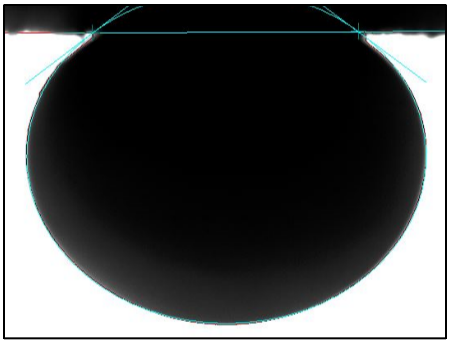
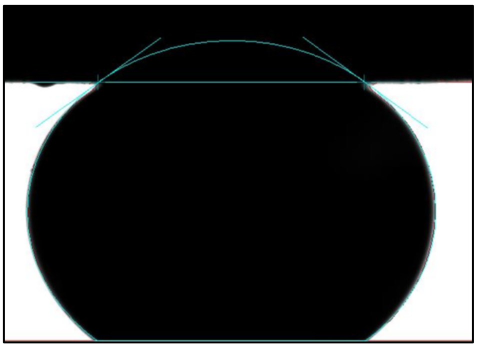


Figure 30. After aging in Caspian Sea for 48-hrs



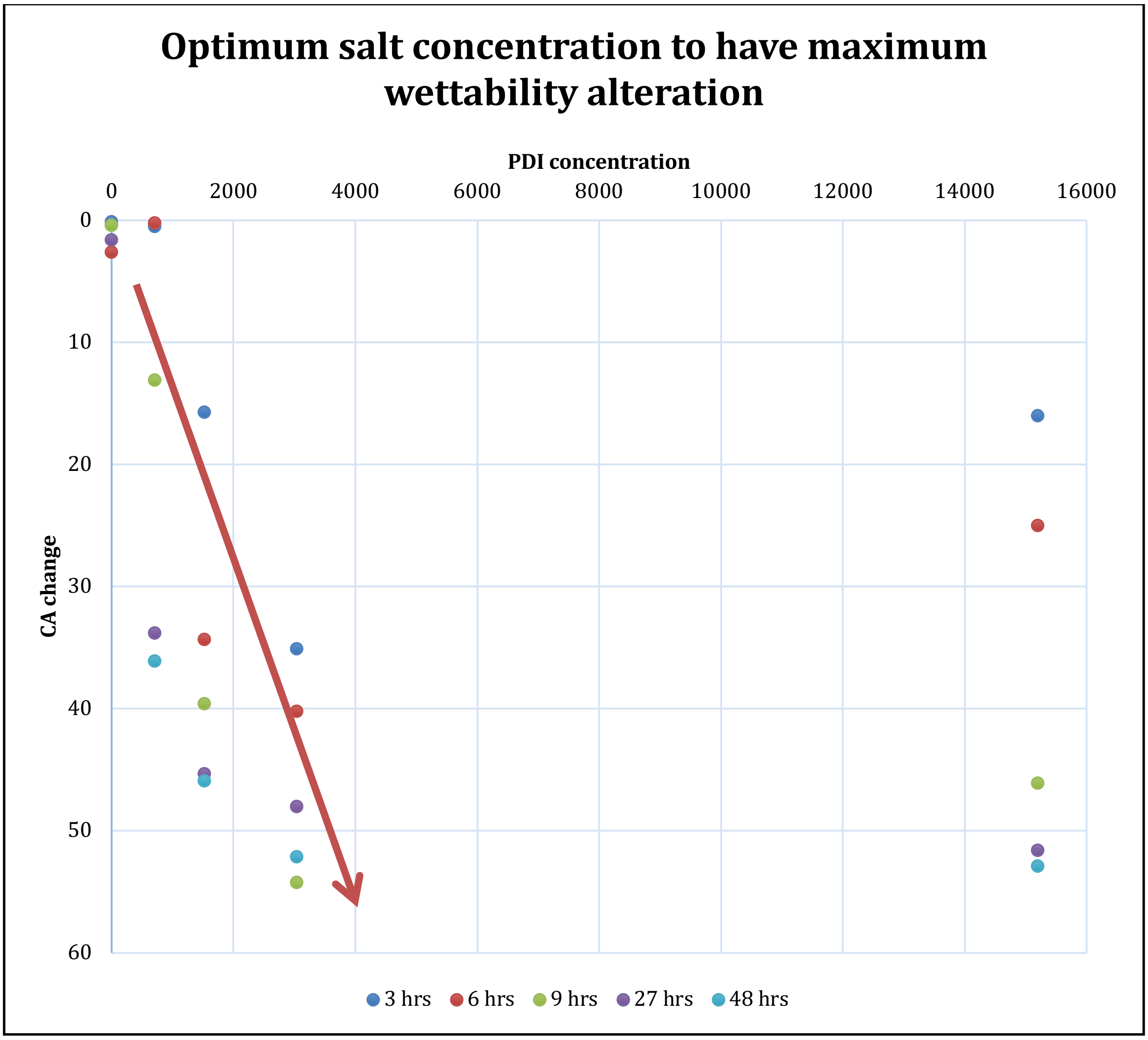


Figure 31. Optimum salt concentration to have maximum wettability alteration

As was described before, by reducing the salt concentration, it is possible to have higher contact angle change between the oil droplet and rock surface. The same conclusion was reached by Yousef and his research group in 2010. Moreover, very diluted fluids containing little salt are not efficient in modifying the wettability state of the system, and could not result in any contact angle change, as for example deionized water. Figure 31 also clearly demonstrates that brines with high salt concentration are not efficient in contact angle adjustments, due to presence of a high number of inactive ions not participating in the alteration process, as Na^+ and Cl^-, that prevent active ions from approaching to the surface. Thus, there is an optimum salt concentration that is required to have the highest contact angle shift, and also a certain concentration range that could activate the wettability alteration process. A similar trend is revealed at each time interval. From Figure 31, at all-time intervals brines with increasing TDS concentration from 0 to 3000 ppm resulted in increased CA change. However, for brine with TDS of 15000 ppm contact angle measured at the same time intervals showed a much lower CA change. This does not mean that increasing the TDS concentration of brine will always result in increasing contact angle change. There is an optimum range of salt concentration that could have a highest shift in CA. Moreover, to see an immediate response to the low salinity brine injection, the minimum total salt concentration should not be less than 850 ppm.

Caspian Sea water, 5 times diluted, and 10 times diluted brines all showed promising results, as all of them were able to vary the wettability of carbonate rock surface and change initial contact angle from 86° to 35° – 40° after 2 days. However, the rate of wettability alteration in all cases was different. As an example, 5 times diluted CSW was able to have its maximum CA shift just in 9-hrs. While it took two days for Caspian Sea water to reach the same shift in CA. the speed of alteration in the case of 10 times diluted brine was the slowest compared to other cases. An important conclusion can be drawn from these contact angle measurements results, Caspian Sea water without doing any modifications can be utilized as a low salinity injection brine during EOR projects. Since the objective of the current work was to find the most optimal brine solution that can have a maximum wettability alteration of the surface in the shortest possible time, 5 times diluted CSW was chosen as the basis to study ions effect. Moreover, contact angle measurement results revealed that no significant changes occurred after 9-hrs aging in engineered brines. For this reason, further laboratory investigation was done for shorter time period just to see and analyze the effect of certain ions on the rate of wettability alteration.

Figure 32 shows an early time contact angle change. In all brine solutions, the angle between the oil and rock surface is progressively increasing, indicating the detachment of an oil droplet and changing the carbonate surface to the more water-wet state. While there is no positive increase in contact angle during the late time analysis as shown in Figure 33. On the contrary, the angle change is slightly decreasing, which probably indicates the system’s stabilization. This is a valuable finding in this study, as the objective of this work aimed to see how quickly the CBR system can have a response to the invasion of engineered water. Contact angle measurement results confirm that even a small amount of time, in this case, 9-hrs, is more than enough to observe an immediate response to engineered water injection.

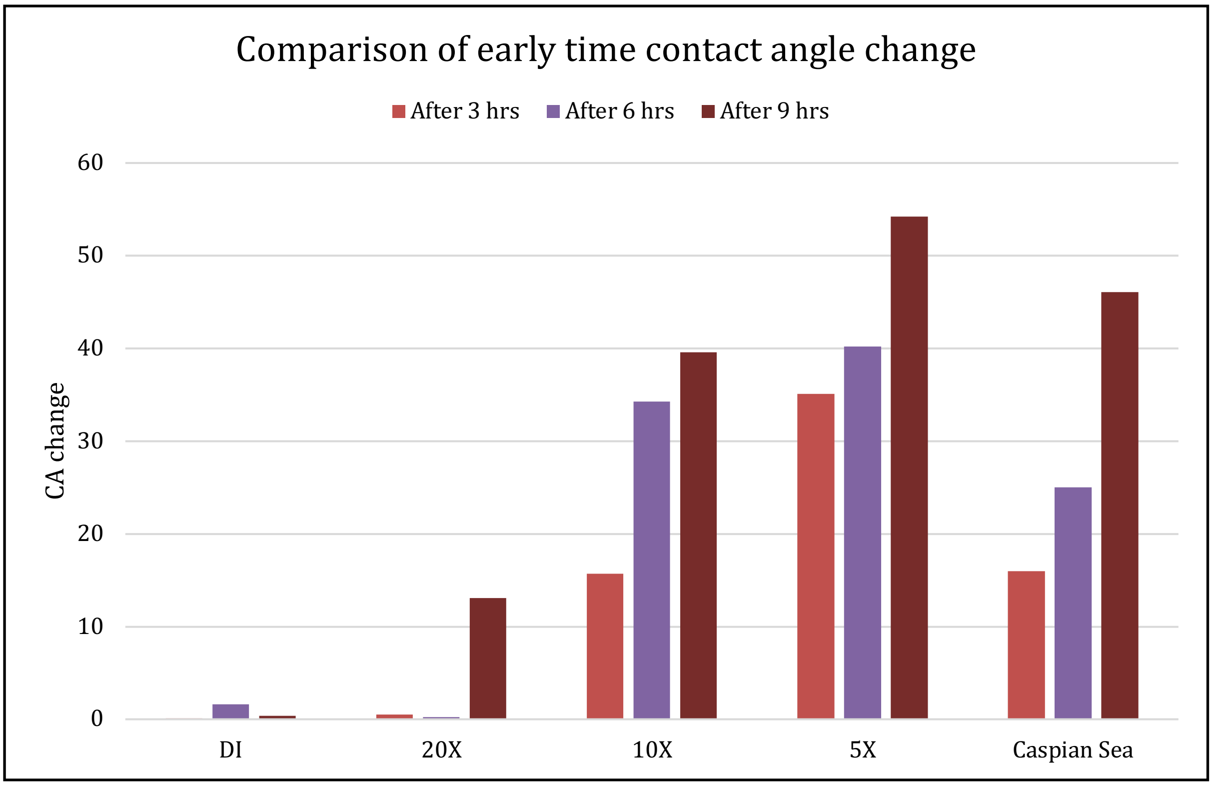


Figure 32. Early time CA change

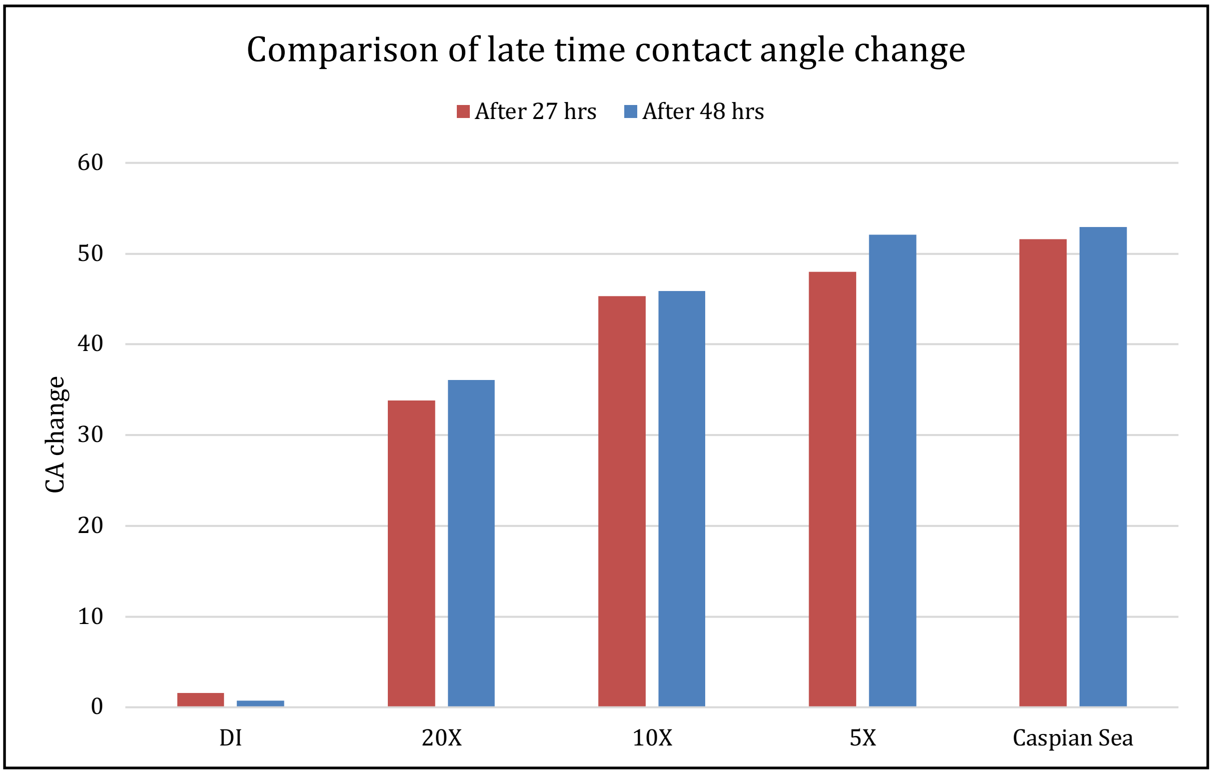


Figure 33. Late time CA change

5.2 Effect of ions on contact angle measurements

The purpose of studying the effect of individual ions was to investigate which of them are the most efficient and whether it is possible or not to further change the wetting state of the carbonate rock surface. At the first stage, the most optimum dilution ratio was identified to be 5 times diluted Caspian Seawater. Five different solutions were prepared to examine the effect of Mg^{+2}, Ca^{+2}, and SO_4^{-2} ions on the rate of wettability alteration. The idea was to keep the total dissolved solid amount to be approximately the same, in the range of 5000-5500 ppm, in each brine in order to eliminate the effect of salinity. For this purpose, to see the effect of certain ions at a time, their concentrations were increased by 5-7 times. For example, in 5X_Mg brine, the concentration of magnesium ion was increased 5 times, in 5X_Ca brine, the concentration of calcium ion was increased 7 times, etc. In 5X_Mg_SO4 and 5X_Ca_SO4 brines sulfate ions were increased simultaneously with calcium or magnesium ions respectively to see the effect of counterions. The exact chemical composition of brines was analyzed by Ion Chromatography and results are presented in Table 7 in the Materials and Methodology part.

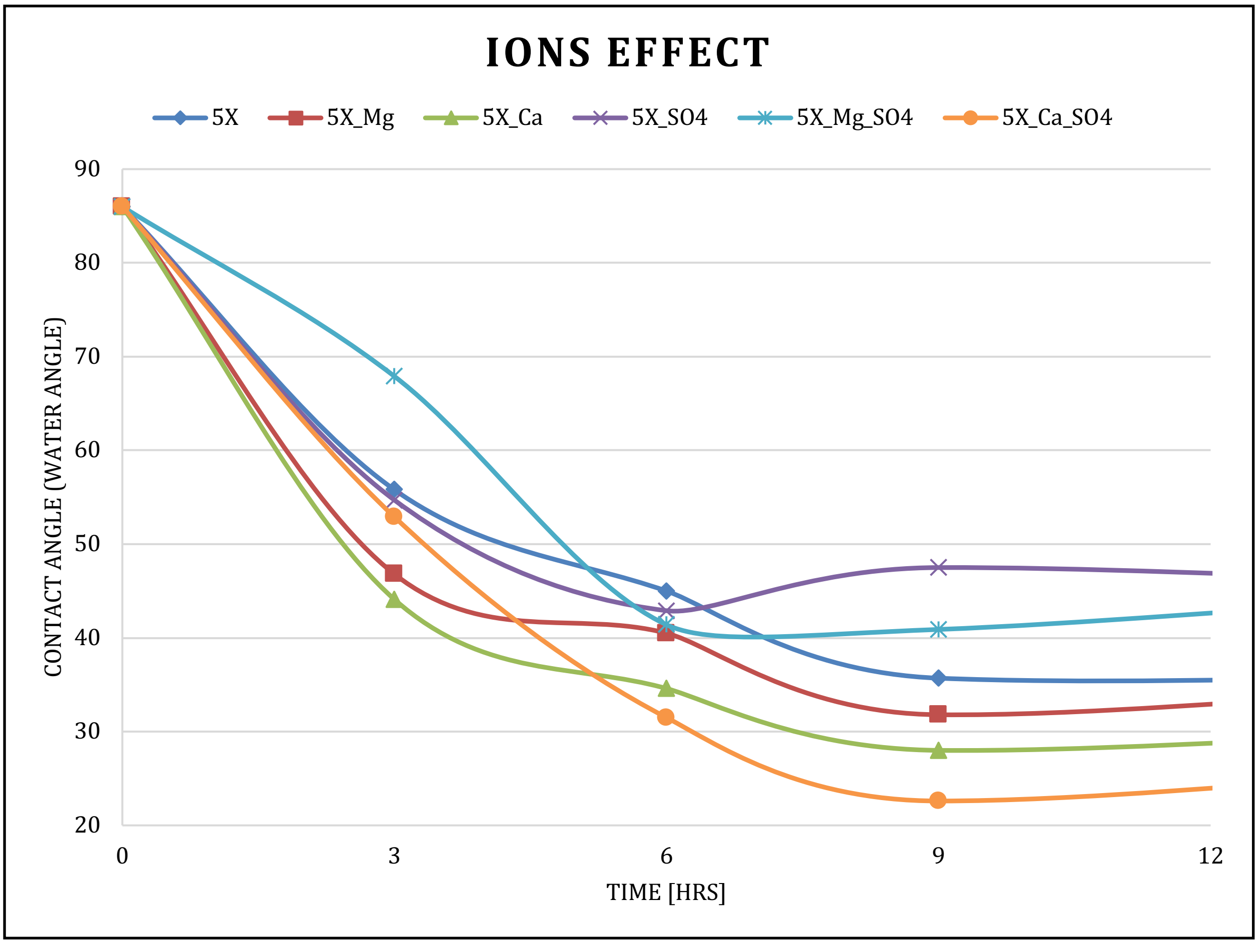


Figure 34. Effect of individual ions on rate of CA alteration

Cores slices were placed into the containers with brine, following the same procedure as mentioned previously in the case with dilution. Contact angle measurements between an oil drop and rock surface were taken after 3, 6, and 9 hrs. Figure 34 demonstrates the results of CA as a function of time. To distinguish the impact of certain ion, results can be compared with 5X brine. It was possible to highlight several key points. Firstly, it can be concluded that 5X_SO4 and 5X_Mg_SO4 brines did not have any further effect on CA. All of these brines reached 40 – 45° angle after two days of aging. The same contact angle was reached by 5X brine.

Whereas in 5X_Mg, 5X_Ca, and 5X_Ca_SO4 brines, a further decrease was observed compared to 5X results. Moreover, the rate of the wettability alteration process caused by 5X_Mg, 5X_Ca, and 5X_Ca_SO4 brines was faster. As an example, it was possible for 5X brine to reach a 35° of contact angle within 9-hrs, but it took only 6-hrs for 5X_Mg, 5X_Ca, and 5X_Ca_SO4 brines to reach the same change in CA.

Secondly, while comparing the results of two brines, 5X_Ca and 5X_Ca_SO4, it is possible to emphasize on catalytic properties of sulfate ion. However, the presence of only sulfate ions is not enough, as there is a need for active cations, such as magnesium or calcium. In our case, calcium is more active for wettability alteration. For example, 5X_SO4 brine did not result in any positive angle change compared to 5 times diluted brine.

The same trend as previously was observed while studying the effect of dilution. All brine solutions resulted in their highest CA change during the first 9-hrs of the experiment. Aging for a longer time did not result in an effective CA modification. To emphasize this feature, three bar charts were created demonstrating the effect of early time and late time contact angle change progress.

In conclusion, among all brine solutions, 5 times diluted CSW with a spiked concentration of Ca^{+2} and SO_4^{-2} simultaneously resulted in the highest change from 86° to 22°, indicating strongly water-wet conditions. These ions were able to decrease the contact angle for an additional 12°. For this reason, 5X_Ca_SO4 brine was chosen to be the most optimum brine and will be used as engineered water in spontaneous imbibition experiments.

5.3 Ion Chromatography analysis

It was possible to see the positive effect of all smart brines on wettability alteration. And the objective of this chapter is to provide evidence and support on the underlying mechanism of smart water on carbonate formations. For this purpose, water samples, where core slices were aged, were collected for ion chromatography (IC) analysis to understand the distribution of ions during aging in smart water. The results of the geochemical properties of brine taken at the same time intervals as contact angle measurements are illustrated in Figure 35 - 41. The dashed lines correspond to initial ion concentrations. The chapter is divided into 6 sub-sections where all brines mechanisms were discussed separately.

2.3.1 Brine 5X_Ca_SO4

This section provides the IC results of 5X_Ca_SO4 brine chosen for spontaneous imbibition test. The change of ion concentration in ppm vs time is illustrated in Figure 35.

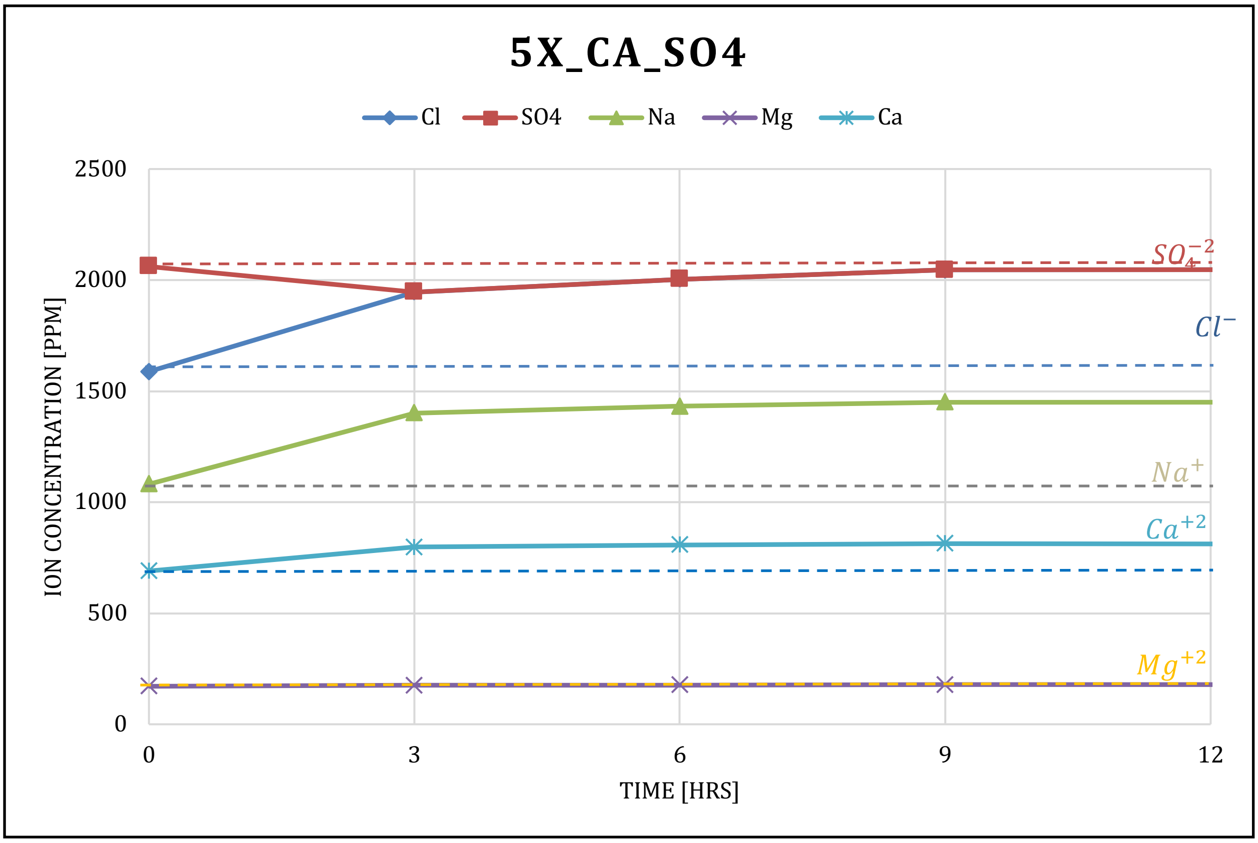


Figure 35. 5X_Ca_SO4 brine IC results

In Brine 5X_Ca_SO4, ions were normalized mostly after 9-hrs being in contact with the CBR system. This indicates that the ion-exchange mechanism happened during this time interval, which is in agreement with CA results, where the maximum possible shift happened during the first 9-hrs. For this reason, in a discussion of ion exchange, only the first time period is considered. As mentioned in the methodology section core slices were first aged in the formation brine, which does not contain sulfate ions. Illustration of initial ion distribution is presented in Figure 36-a.

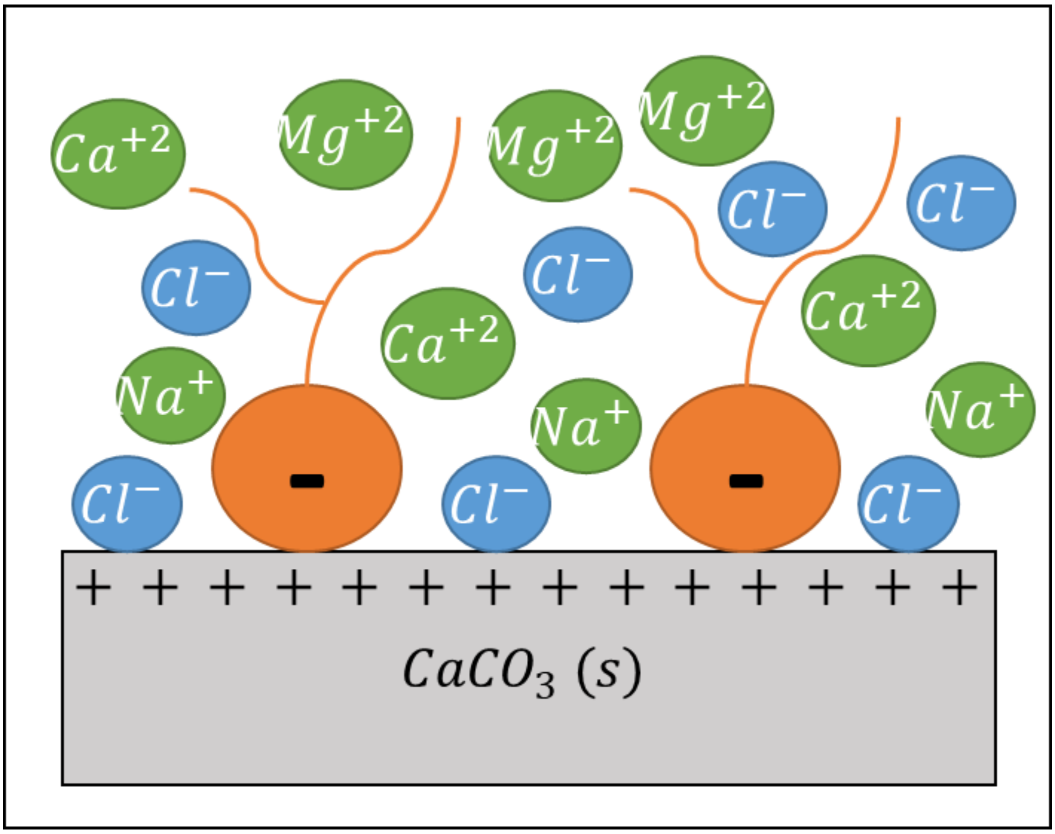


Figure 36. Initial ion distribution

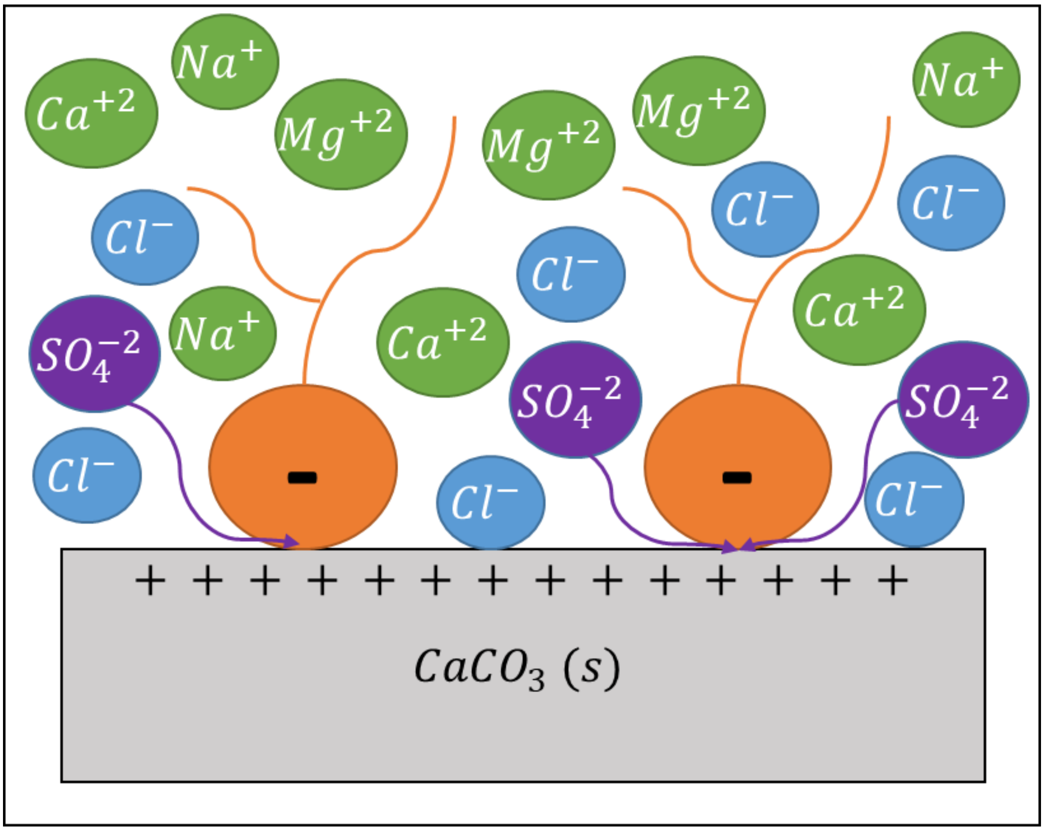


Figure 36-b. Adsorption of sulfate ions

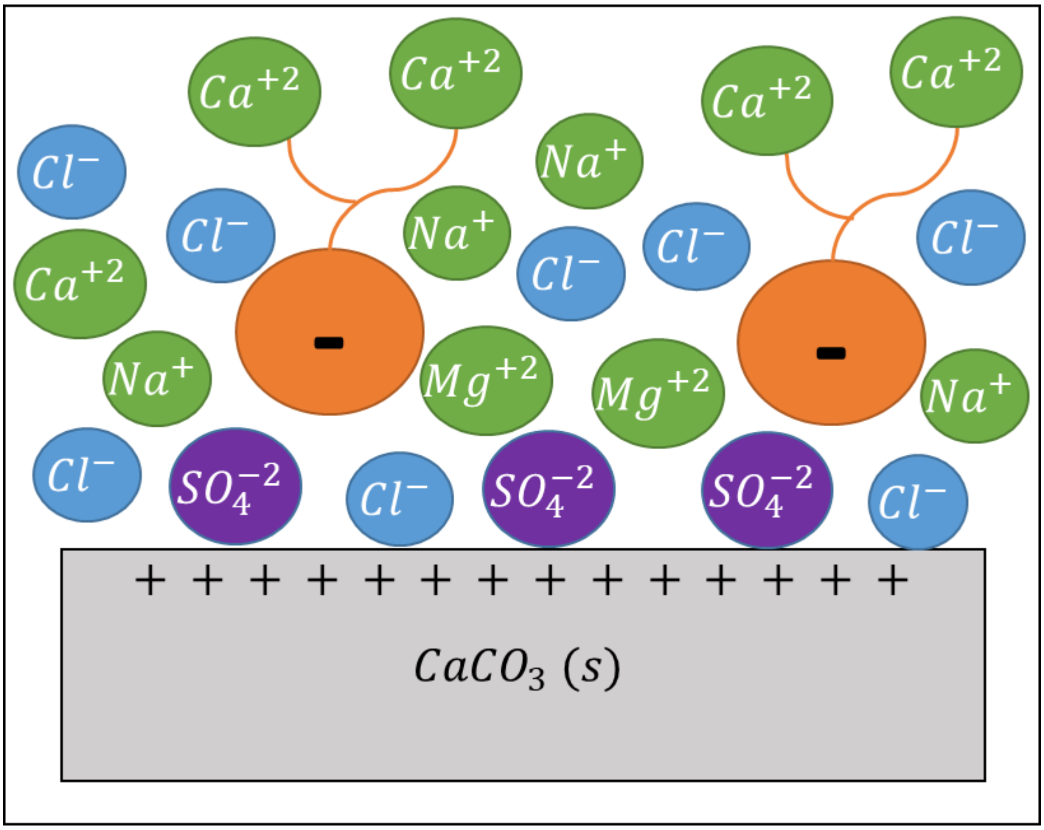


Figure 36-c. Release of oil components as $(RCOO)_2Ca$ compound.

Once, engineered 5X_Ca_SO4 water was injected, a decrease in sulfate concentration can be observed as seen from Figure 35. This is probably due to higher adhesion of sulfate ions to the rock surface compared to oil components, as shown in Figure 36-b. As a result, the oil component is released and dissociated in water according to Reactions 1-2, while SO_4^{-2} remained stuck to the carbonate rock surface.

1. $RCOOH_{(o)} \leftrightarrow RCOOH_{(aq)}$

2. $RCOOH_{(aq)} \leftrightarrow RCOO^-_{(aq)} + H^+$

The release of H^+ ions caused pH decrease, indicating that the environment has become acidic. pH measurements showed the same trend. Finally, oil components coupled with Ca^{+2} left the system as $(RCOO)_2Ca$ compound, as shown in Reaction 3 and Figure 36-c.

3. $Ca^{2+}_{(aq)} + 2RCOO^-_{(aq)} \leftrightarrow (RCOO)_2Ca_{(aq)}$

Mg^{+2} ion concentration did not change during the whole experiment, suggesting that this ion was not participating in the MIE process or not active in these conditions. Then, to compensate for the decrease of calcium ions due to its release as $(RCOO)_2Ca$ compound, most likely carbonate dissolution took place, as written in Reaction 4.

4. $CaCO_3\ (s) \rightarrow\ Ca^{+2}(aq) +\ {CO_3}^{-2}\ (aq)$

Carbonate dissolution produces calcium ions, yielding its overall increase. The same trend can be observed in Figure 35, where calcium ion concentration is increased during the first 9-hrs. Now the rock surface became more negatively charged (CO_3^{-2}), which in turn leads to more repulsion of oil component.

The fluid was injected into the CBR system always had much lower salinity concentration compared to formation brine. Therefore, to finally attain a chemical equilibrium in the system there was a substantial increase in Na^+ and Cl^- ions almost in all cases. Na^+ and Cl^- ions from formation brine inside the rock were going to the low salinity water.

From Figure 35, noticeable sulfate concentration decrease can be observed only during first 3-hrs. Therefore, another reaction for MIE mechanism, where sulfate ions concentration is not much affected during 6 – 9 hours' time interval, is shown below:

5. $RCOO^{-} - CaCO_3\,(s) + Ca^{+2} + SO_4^{-2} \rightarrow CaCO_3\,(s) + RCOOCa^{+} + SO_4^{-2}$

The proposed mechanism is in agreement with suggested by Zhang et al in 2006. Moreover, the work done by Su and his group also showed the effect of Ca^{2+} on wettability alteration is greater than that of Mg^{2+} at lower temperatures. (Su et al., 2019)

2.3.2 Brine 5X_Mg_SO4

This section provides the IC results of 5X_Mg_SO4 brine. The change of ion concentration in ppm vs time is illustrated in Figure 37.

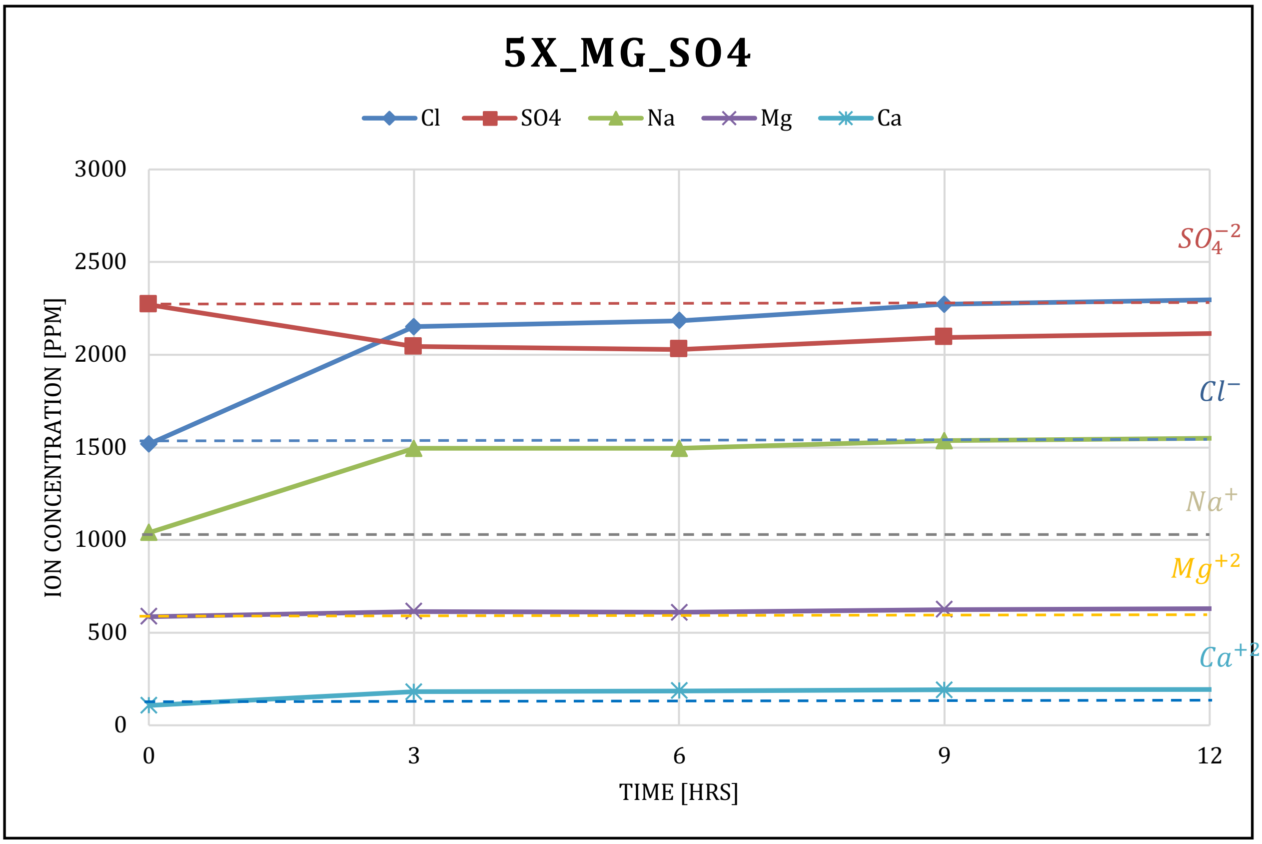


Figure 37. 5X_Mg_SO4 brine IC results

The same mechanism of oil release could be proposed for 5X_Mg_SO4 brine. Firstly, we had sulfate ions reduction, that initiated the multi-ion exchange process. The concentration of calcium increased indicating rock dissolution. However, the extent of MIE is smaller compared to 5X_Ca_SO4, as the initial concentration of calcium in the brine was much lower. Besides, the main difference that occurred, in this case, was that magnesium concentration started to increase slowly after 9-hrs of interaction. This was the only case where Mg^{+2} ions were also active in MIE, as in all other cases there was no change. Several studies have shown the activity of magnesium ions only at high temperatures, specifically above 80 °C. (Zhang et al., 2006) Therefore, it can be concluded that both ions, magnesium, and calcium are active. But as in our experiments, the temperature was comparatively low, the effect of magnesium can be hardly noticed. The process of exchange with magnesium was slower at low temperatures.

2.3.1 Brine 5X

This section provides the IC results of 5X brine. The change of ion concentration in ppm vs time is illustrated in Figure 38.

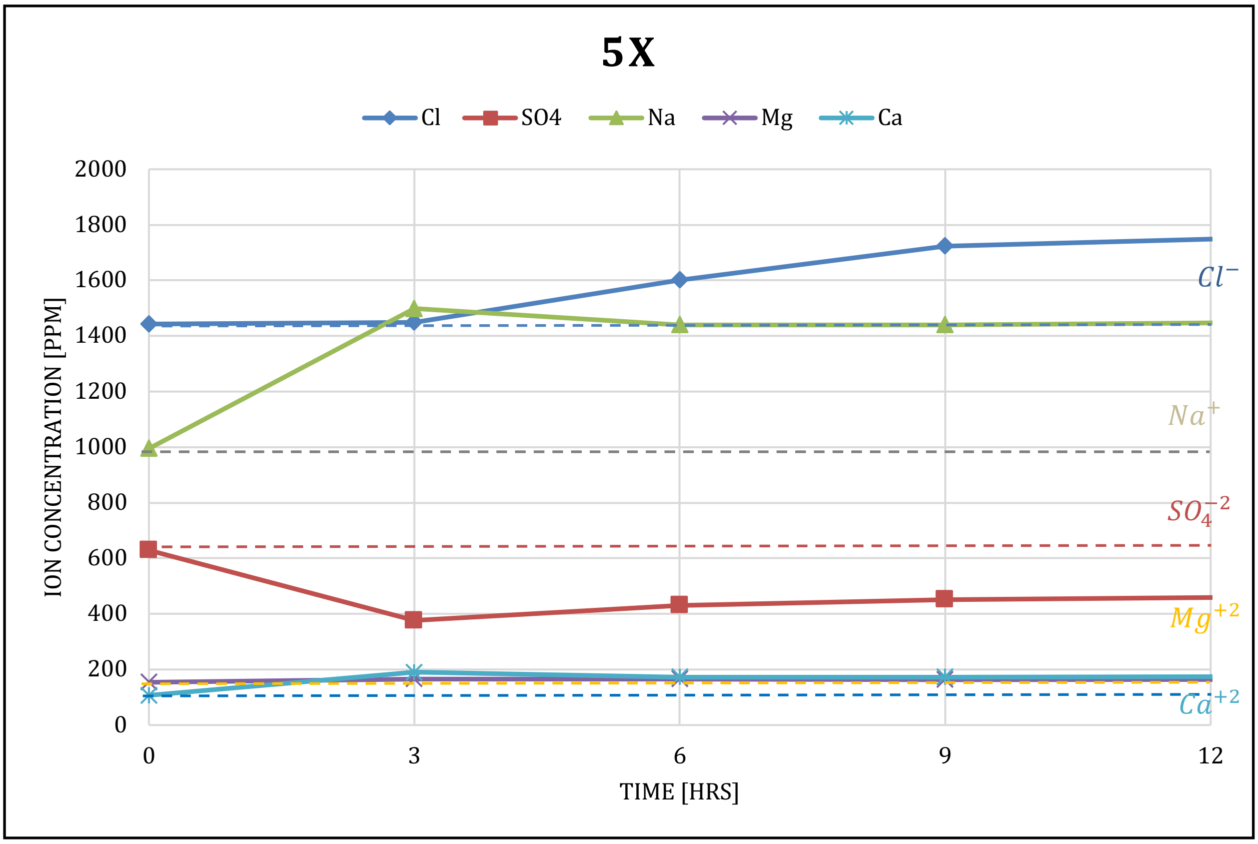


Figure 38. 5X brine IC results

The trend of ion distribution was the same as in 5X_Ca_SO4 brine, proof that the multi-ion exchange mechanism took place. However, the initial amount and consumptions of SO_4^{-2} and Ca^{+2} were much lower than in 5X_Ca_SO4 case. As a result, the rate and extent of wettability alteration were lower. Same as previously, Na^+ and Cl^- ions concentration increased, indicating an exchange with formation brine to reach chemical equilibrium.

2.3.2 Brine 5X_SO4

This section provides the IC results of 5X_SO4 brine. The change of ion concentration in ppm vs time is illustrated in Figure 39.

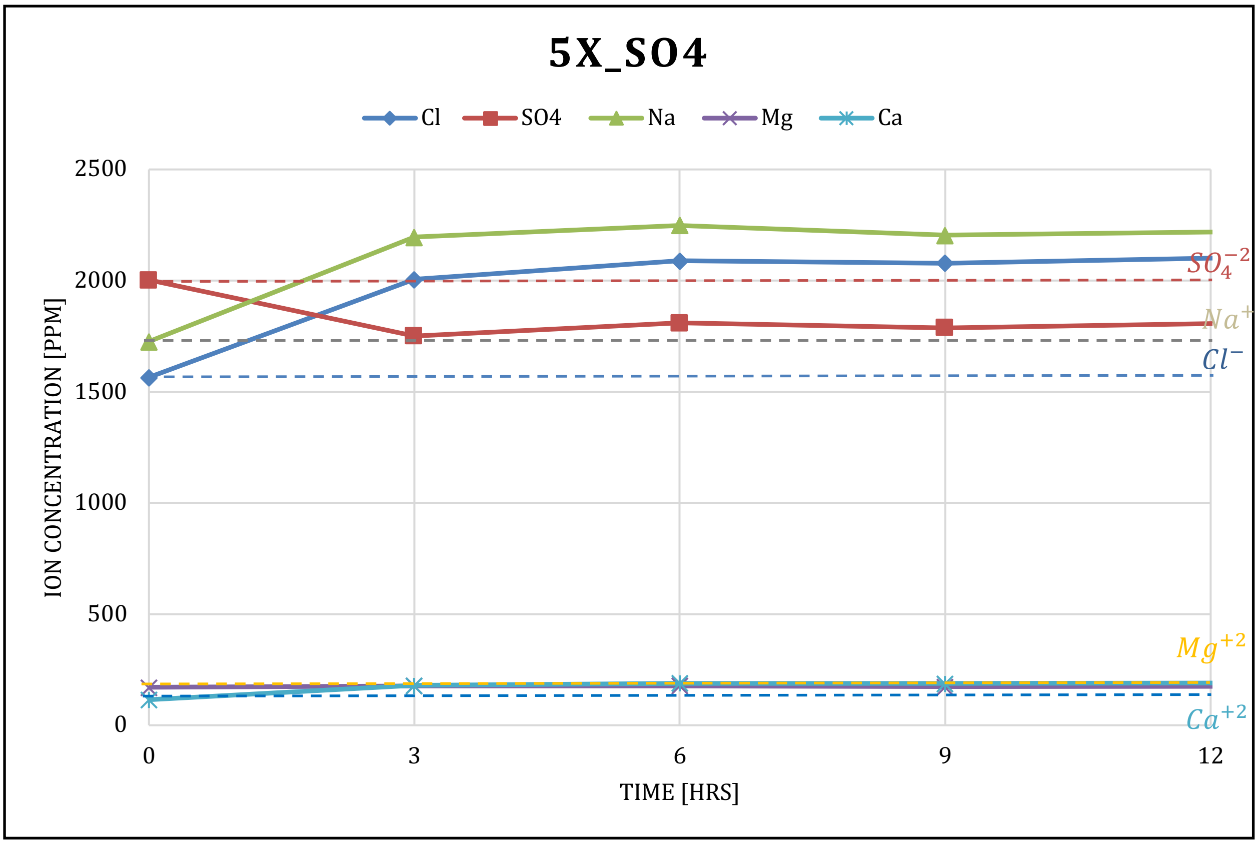


Figure 39. 5X_SO4 IC results

The trend of ion distribution was the same as in 5X_Ca_SO4 and 5X brine, indicating the same multi ion-exchange mechanism, where the release of carboxylic material was caused by adsorption of sulfate ions. In comparison with 5X brine, the addition of sulfate ions does not result in any additional CA change. It can be concluded that the presence of sulfate ions alone was not enough to enhance wettability alteration.

2.3.3 Brine 5X_Ca

This section provides the IC results of 5X_Ca brine. The change of ion concentration in ppm vs time is illustrated in Figure 40.

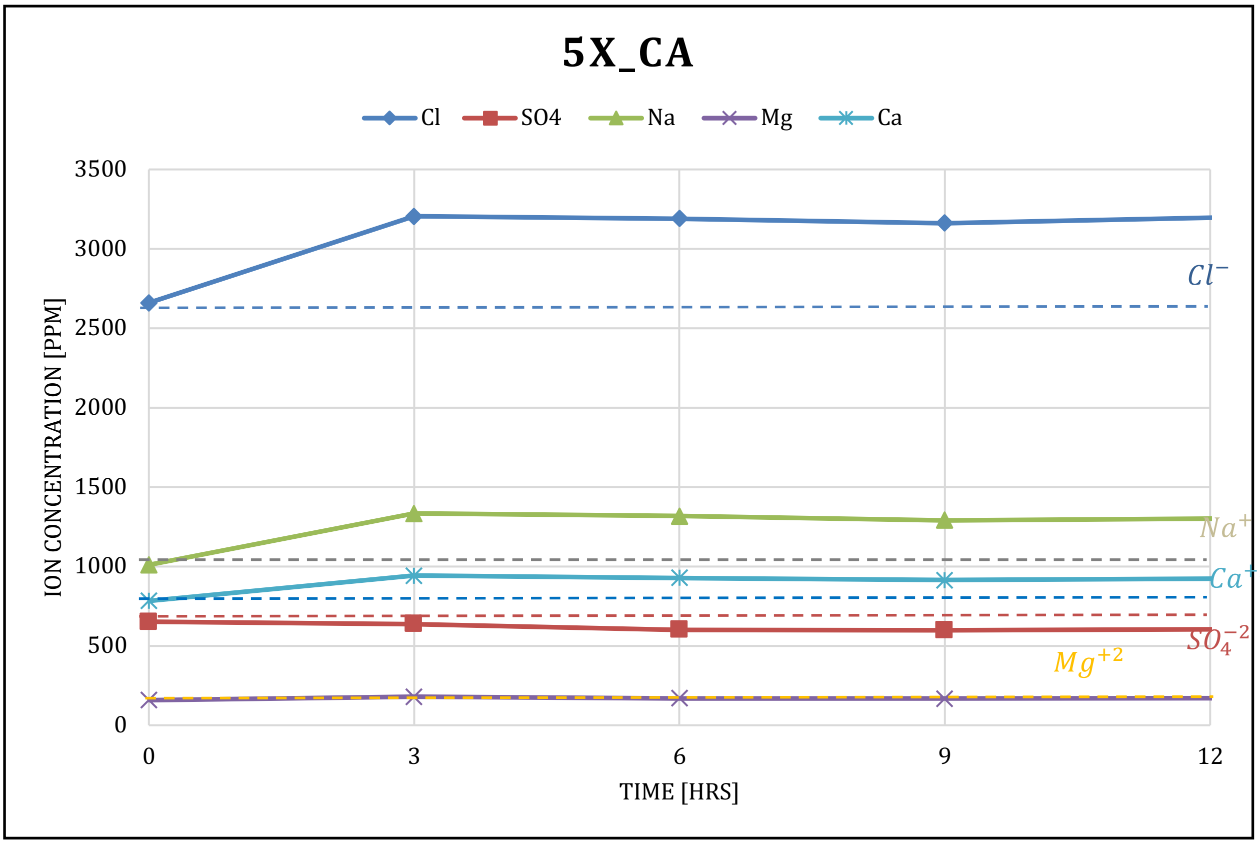


Figure 40. 5X_Ca brine IC results

The trend of ion distribution was the same as in 5X_Ca_SO4 brine, proof that a multi ion-exchange mechanism took place. Although in both cases 5X_Ca and 5X_CA_SO4 the decrease of sulfate ions was less compared to other cases. However, still, the ion exchange process can be observed from the results of contact angle measurements. So, another possible reaction for MIE mechanism, where sulfate ions are not much affected, as shown below:

5. $RCOO^- - CaCO_3\,(s) + Ca^{+2} + SO_4^{-2} \rightarrow CaCO_3\,(s) + RCOOCa^+ + SO_4^{-2}$

The concentration of Na^+ and Cl^- ions increased, indicating the exchange with formation brine to reach chemical equilibrium.

2.3.4 Brine 5X_Mg

This section provides the IC results of 5X_Mg brine. The change of ion concentration in ppm vs time is illustrated in Figure 41.

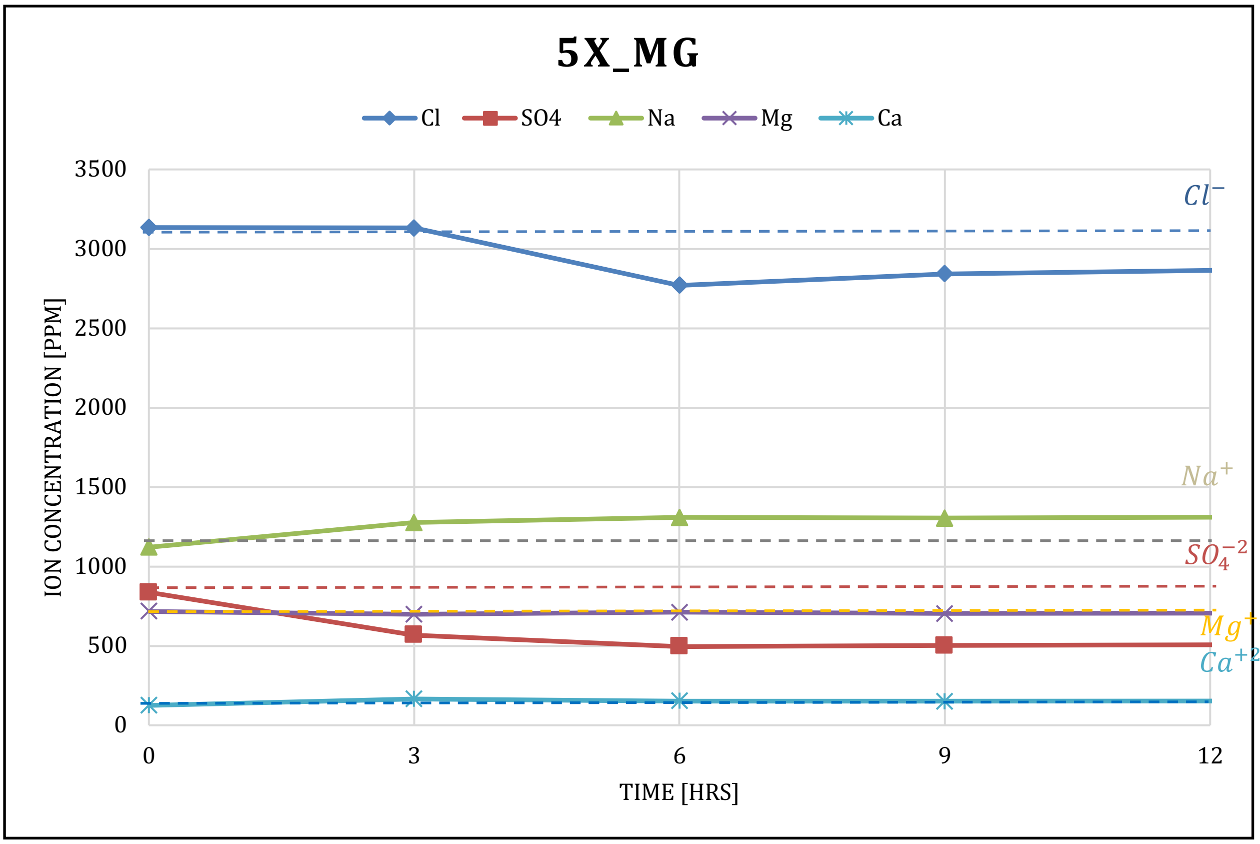


Figure 41. 5X_Mg brine IC results

In the case of 5X_Mg brine, the trend of ion distribution was different from previous cases. There was no change in Mg^{+2} and Ca^{+2} identified. A possible mechanism for wettability alteration was the release of oil components as $RCOONa$ compounds. Firstly, as in all previous cases, there is an adsorption of sulfate ions due to their higher affinity to the carbonate rock surface. A decrease in sulfate concentration is clearly shown in Figure 41 confirming this. As the concentration of Mg^{+2} and Ca^{+2} did not change, the release of carboxylic material may occur with Na^+ ion. In general, the MIE mechanism, in this case, was very weak. As was discussed before, the magnesium ions are not as active as calcium ions at the temperature of our tests. In conclusion, from ion chromatography results several points can be highlighted. First, the main underlying mechanism behind the smart water effect was suggested to be the multi-ion exchange. The proposed mechanism requires adsorption of SO_4^{-2} ions in all cases. For oil release, there was a need for cations, as Ca^{+2}. Sulfate ions play a catalytic role during wettability alteration as was proved before based on CA measurements. Mg^{+2} becomes active at higher temperatures.

5.4 pH analysis

The objective of this section was to study the change in pH change during the aging in different smart brines to confirm the mechanisms involved in the oil recovery processes. For this purpose, during the aging process, samples of water were collected, and their pH was measured at the same time as contact angle measurements. A plot of pH versus time is presented in Figure 42.

Generally, the brines showed a consistent decrease in pH which was suggested to be due to the washing of acidic crude oil components into the brine. There are two possible mechanisms to describe the change in the pH: 1. Surface ion exchange; 2. CO_2 production. As was discussed before, during surface ion exchange, the oil component dissociates and produces H^+ atoms. This mechanism was first proposed by Austad and his colleagues in 2006. The reactions are provided below. Due to adsorption of sulfate ions into the carbonate rock surface, the oil component is released and dissociates in water by producing hydrogen atom, indicating acidic environment.

$$1.\ RCOOH_{(o)} \leftrightarrow RCOOH_{(aq)}$$

$$2.\ RCOOH_{(aq)} \leftrightarrow RCOO^-_{(aq)} + H^+$$

$$3.\ Ca^{2+}_{(aq)} + 2RCOO^-_{(aq)} \leftrightarrow (RCOO)_2Ca_{(aq)}$$

$$3.\ Mg^{2+}_{(aq)} + 2RCOO^-_{(aq)} \leftrightarrow (RCOO)_2Mg_{(aq)}$$

Moreover, pH decrease can be associated with CO_2 production, reactions are written below.

$$1.\ MgCl_2\ (aq) + CaCO_3\ (s) \leftrightarrow MgCO_3\ (s) \downarrow + CaCl_2\ (aq) + H_2O\ (l) + CO_2\ (g) \uparrow$$

$$2.\ CO_2\ (g) + H_2O \leftrightarrow 2H^+ + CO_3^{-2}$$

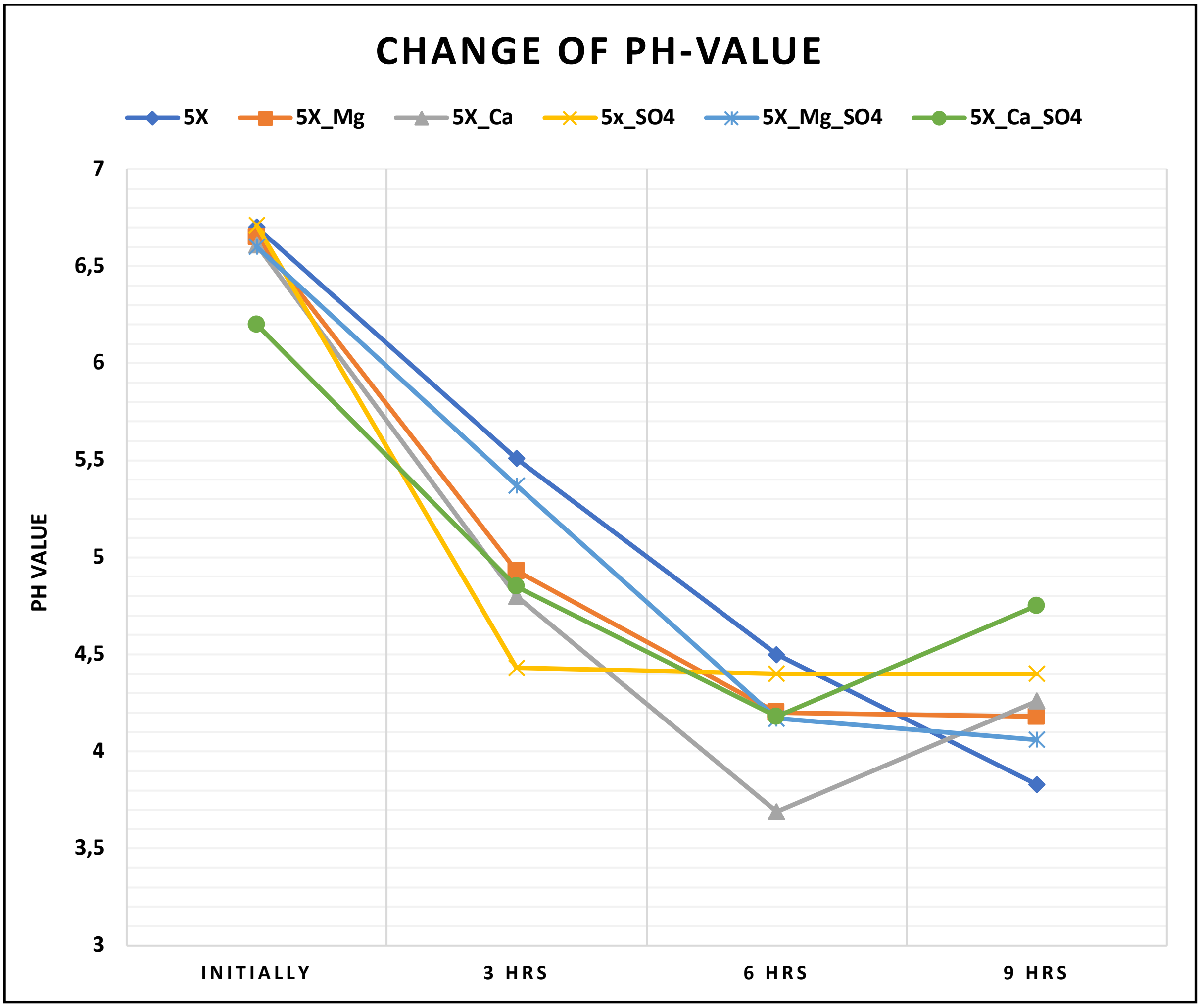


Figure 42. pH change vs time

5.5 Spontaneous imbibition test

The aim of spontaneous imbibition tests was to study the rate of wettability alteration by Caspian Sea water and 5 times diluted CSW with spiked concentration of Ca^{+2} and SO_4^{-2} ions. The test was carried out at 80 ºC. Core 1 was used for CSW and core 2 was used for 5X_Ca_SO4 to eliminate any errors related to additional oil recovery due to higher permeability for 5X_Ca_SO4. Figures 43, 44 demonstrate oil expulsion during SI experiment. The trend of recovery factory versus time is depicted in Figure 45.

Figure 43. Oil expulsion during spontaneous imbibition tests

Figure 44. Oil expulsion during spontaneous imbibition tests

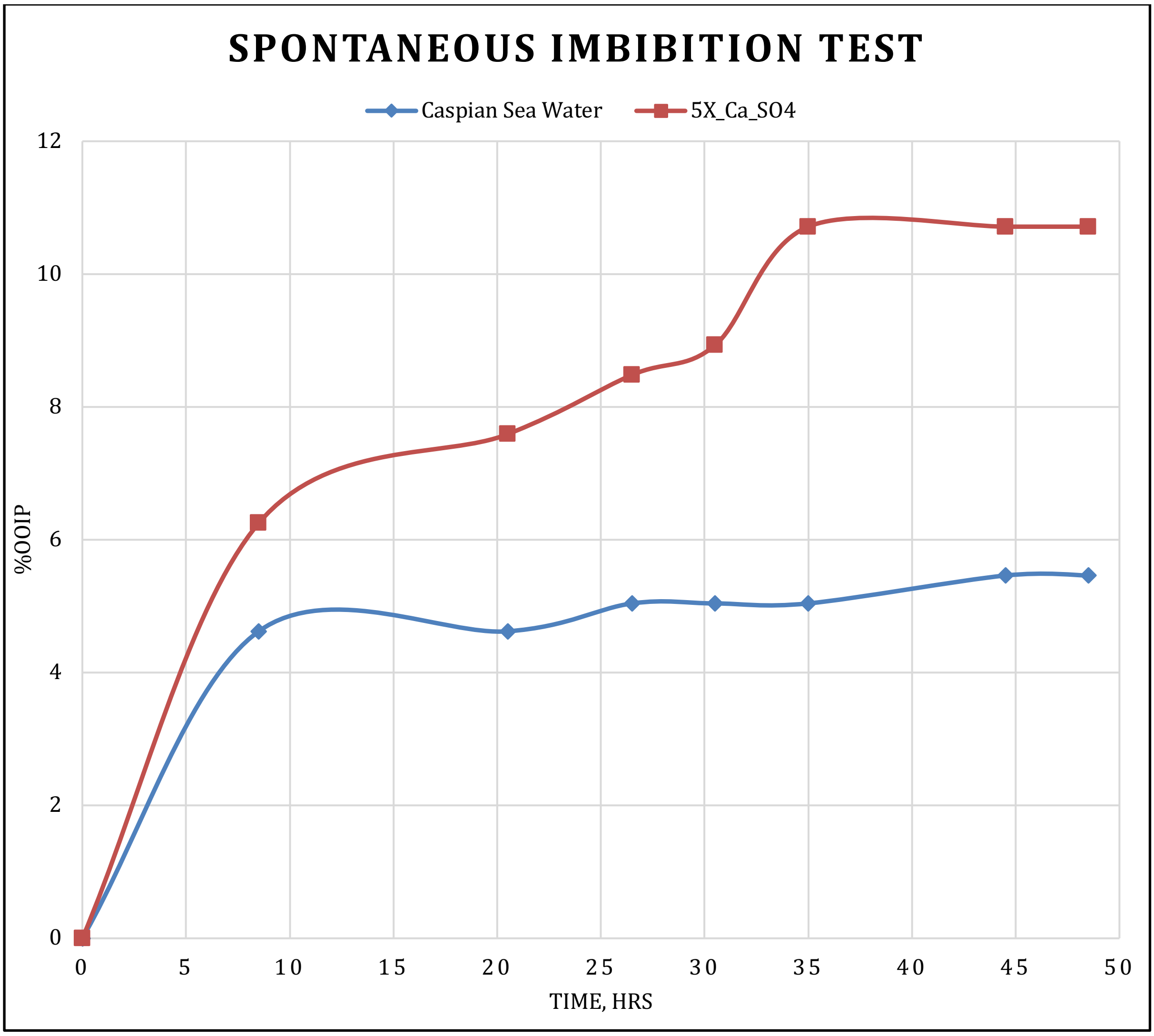


Figure 45. Recovery factor trends by spontaneous imbibition tests

Due to low permeability and heterogeneity of core plugs, and high viscosity of oil, the recovery process occurred relatively slow. For example, it took 30-hrs to reach a plateau in production for both cases. Even though the core with lower permeability was used with 5X_Ca_SO4 as an imbibing fluid, it resulted in the highest oil recovery. The recovery factor (RF) by 5X_Ca_SO4 brine is 10.7%, whereas RF by Caspian Seawater is only 5.5% in two days. Spontaneous imbibition test results confirmed the outcomes of CA measurements that 5X_Ca_SO4 brine is the most favorable brine which can be used in the secondary recovery process.

Another important parameter is the trend of the production curve. First, the imbibition rate is higher at the beginning and decreases as the process proceeds. As the rock becomes more water wet the spontaneous imbibition rate will naturally decline. Moreover, as was mentioned before, there are three main ions involved in the multi-ion exchange process, SO_4^{-2}, Ca^{+2}, and Mg^{+2}. Expulsion of oil form the core is initiated by adsorption of SO_4^{-2} because of its higher affinity.

As a result, desorption of negatively charged oil components makes the carbonate rock surface to become more positively charged. Therefore, repulsive forces between the rock surface and cations (Ca^{+2}, Mg^{+2}) in the brine increases. Finally, in agreement with contact angle measurements, the rate of oil expulsion is doubled when the rock is imbibed with 5X_Ca_SO4 brine compared to Caspian Seawater.

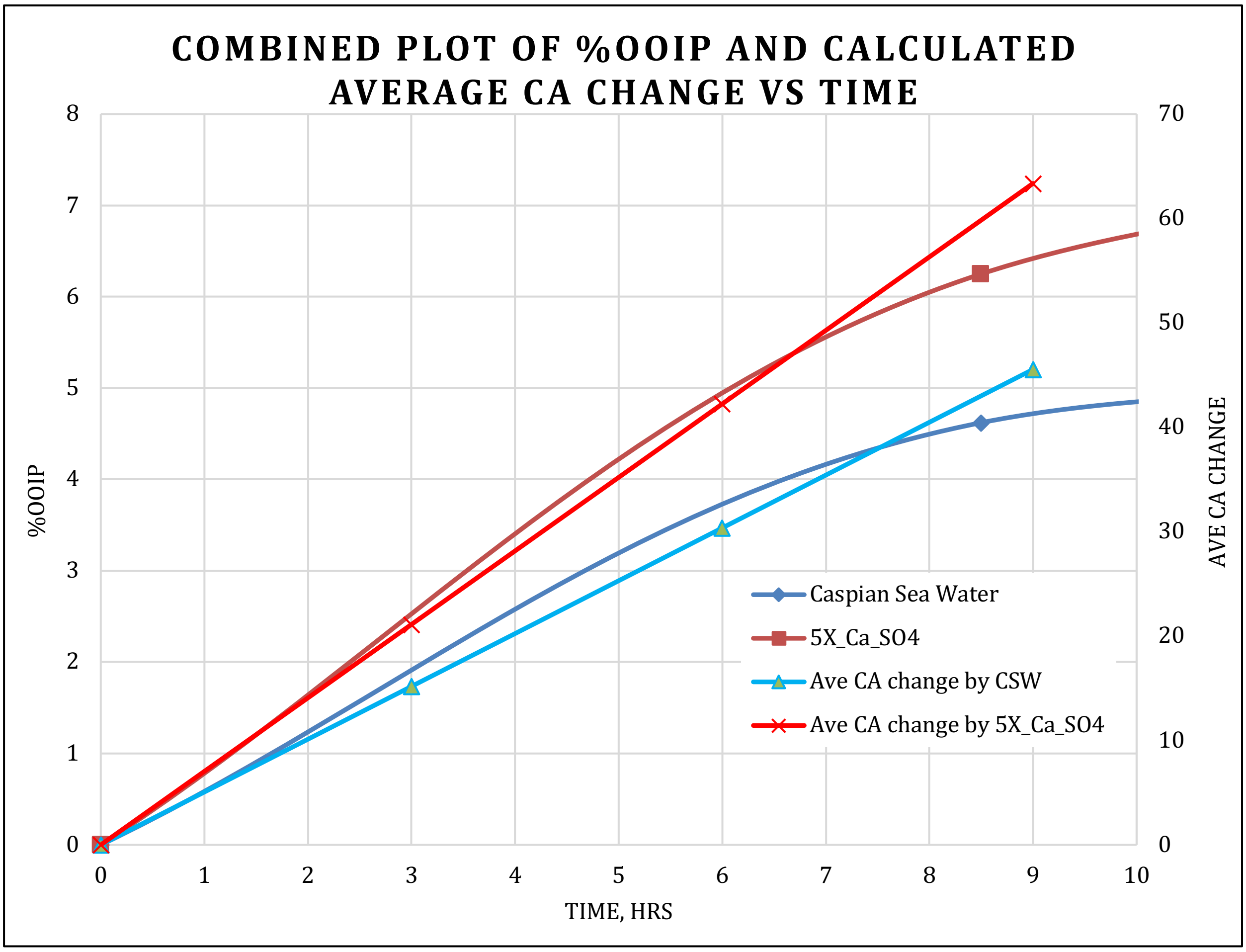


Figure 46. Combined plot of %OOIP and calculated average CA change vs time

To confirm the higher wettability rate caused by 5X_Ca_SO4 brine plot of oil recovery versus time was combined with a calculated average contact angle change as shown in Figure 46. Based on the results of contact angle measurements, CA change per time was calculated for each brine, and an average value was taken to be 5.06°/hour for Caspian Seawater and 7.04°/hour for 5X_Ca_SO4 brines, respectively. Average CA change results reveal that 5X_Ca_SO4 brine is able to shift the initial wettability of the system from the neutral wetting state towards more water-wet much faster that Caspian Seawater. Oil recovery obtained from spontaneous imbibition tests exactly confirm the higher oil production rate caused by 5X_Ca_SO4 as a result of the wettability alteration process.

6. CONCLUSIONS AND RECOMMENDATIONS

The current study has emphasized the impact of SO_4^{-2}, Ca^{+2}, and Mg^{+2} ions in the Caspian Sea engineered water on the rate of wettability alteration in carbonate formations. The objectives of the research were to find the optimum composition of Caspian Sea water by changing its overall salt concentration and to determine ion composition that could result in the highest wettability alteration of the rock surface. Also, different tests such as pH analysis, ion chromatography tests, and spontaneous imbibition were performed to analyze the active mechanism which affects the rate of wettability alteration. The following conclusions can be drawn from obtained results:

- While studying the effect of dilution based on contact angle measurements it was found that deionized water was not effective for wettability alteration. There is a minimum salt concentration required to initiate the process of MIE, which is 850 ppm. In addition, there is an optimum range of TDS concentration have the highest shift in wettability. Finally, 5 times dilution showed the highest wettability change from 86^0 to 34^o.

- While studying the effect of active ions based on contact angle measurements it was demonstrated that simultaneous presence of Ca^{+2} and SO_4^{-2} ions could further change the contact angle to 22^o during 9-hrs of aging. Moreover, all brine solutions resulted in their highest CA change during the first 9-hrs of the experiment. Aging for a longer time did not result in effective CA modifications. Finally, 5 times diluted Caspian Seawater with a spiked concentration of Ca^{+2} and SO_4^{-2} was chosen to be the most optimum brine for carbonate rock surface wettability alteration. At the same time, Caspian Seawater without any modifications was able to achieve the same shift, but the rate of wettability alteration was much lower than in the 1st one.

- Ion chromatography results reveal that the main mechanism behind smart water is a multi-ion exchange, that requires adsorption of SO_4^{-2} ions and cations, as Ca^{+2}. Moreover, results have demonstrated that sulfate ions accelerate the wettability alteration process. The ion exchange occurred mainly during the first 9-hrs, which was in agreement with CA results when wettability alteration happened. Finally, it was shown that Mg^{+2} ions are less active at low temperatures.

- pH measurements showed a decrease during the aging procedure in all smart brines under secondary mode which was related to surface ion exchange at an early time and CO_2 production at a later time of the process.

- It was possible to achieve 5.5% of OOIP recovery by Caspian Seawater and 10.7% by 5X_Ca_SO4 brine under secondary mode during spontaneous imbibition tests. The imbibition rate was observed to be higher at the beginning of the experiment which was related to increased repulsive forces between the rock surface and cations in the brine as oil expulsion proceeds.

- Average CA change results reveal that 5X_Ca_SO4 brine is able to shift the initial wettability of the system from the neutral wetting state towards more water-wet much faster that Caspian Seawater. Oil recovery obtained from spontaneous imbibition tests confirms the higher oil production rate caused by 5X_Ca_SO4 as a result of the wettability alteration process.

- Finally, 5X_Ca_SO4 brine was found to be an optimum composition of Caspian Sea water, as it has the highest average CA change per time of 7.04^o/hour. Hence, the highest wettability rate caused by 5X_Ca_SO4 also resulted in faster oil production by spontaneous imbibition test.

Recommendations:

- To carry out forced imbibition tests by core flooding experiments to see incremental oil recovery

- To design an optimized core flood scheme in a secondary recovery mode, considering short-time response of the system

- To model and upscale the current work to the field scale.

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