Experimental Design of “Hybrid Low Salinity Water Flooding and Low Salinity Surfactant Flooding” Enhanced Oil Recovery Method

by

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Originality Statement

I, Aigerim Sekerbayeva, 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 15.04.2020

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Abstract

The objective of the current study is to design a novel hybrid enhanced oil recovery (EOR) method by combining low salinity water (LSW) and low salinity surfactant (LSS) flooding techniques. Alteration in salinity and ions composition of injected brine, type of surfactant, and concentration of surfactant affect the performance of the LSW/LSS approach. In this study, different experiments have been done to screen the smart water with altered ionic composition and surfactant for the optimized performance in conditions of Kazakhstani carbonate oil fields. Different experimental studies have been conducted to analyze the effect of engineered brines, prepared from the Caspian Seawater (SW) on wettability alteration, and the effect of surfactants on development of oil/water microemulsion phase. Contact angle measurements, stability tests, and phase behavior analysis were done to identify the most effective hybrid brine/surfactant formulation to affect capillary forces. Changing to more water-wet state and creation of the middle phase were the main criteria to select the best-engineered brine and anionic surfactant. The efficiency of the developed hybrid method as an EOR approach to displace oil was studied by coreflooding tests.

The largest alteration towards the water-wet condition was recorded at 10 times dilution of the Caspian Sea (SW) with 3- and 6- times spiked calcium and sulfate ions, respectively (10xSW-6SO4, Mg, 3Ca). Among various anionic surfactants screened Soloterra-113H (Alkyl Benzenesulfonic acid) showed the best solubilization ratio, aqueous stability, and Winsor type 3 microemulsions. Thus, in the next stage, a combination of the optimized brine and screened surfactant was analyzed. The wettability alteration by the hybrid method was more compared to the standalone LSW which was confirmed by 10 degrees difference in contact angle measurement. Also, in terms of solubility and creation of the middle phase, the combined method was beneficial and the microemulsion phase constituted nearly 40% of the total height of the oil/brine column. Promising results from the coreflooding test on the oil-wet carbonate core sample was obtained. Recovery factor after injection of formation water was 52%, and it increased to 61% after optimized LSW injection. Finally, after switching to the engineered brine/surfactant, the recovery factor reached 70% that proves the efficiency of the hybrid method. To sum up, the proposed combined method works better than each standalone EOR method due to the higher alteration in capillary number by changing wettability and reduction in IFT, which leads to the higher oil recovery.

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ABBREVIATION

Aging Cell Apparatus	ACA
Calcium ion	Ca^{2+}
Calcium chloride dihydrate	$CaCl_2.2H_2O$
Caspian Seawater	SW
Celsius degree	^0C
Chloride ion	Cl^-
Computational fluid dynamics	CFD
Critical micelle concentration	CMC
Crude oil, brine, and rock	CBR
Decyltrimethylammonium bromide	$C_{12}TAB$
Disodium didecyldiphenylether	DADS
Enhanced Oil Recovery	EOR
Ethylene diamine tetraacetic acid	EDTA
High Salinity Water	HSW
Interfacial tension	IFT
Low salinity water flooding	LSW
Low salinity surfactant flooding	LSS
Magnesium ion	Mg^{2+}
Magnesium chloride	$MgCl_2$
Magnesium chloride hexahydrate	$MgCl_2.6H_2O$
Multi-component ionic exchange	MIE
Oil originally in place	OOIP
Pore volume	PV
Sodium bicarbonate	$NaHCO_3$
Sodium carbonate	Na_2CO_3
Sodium chloride	NaCl
Sodium Dodecylbenzene Sulfonate	SDBS
Sodium ion	Na^+
Sodium sulfate	Na_2SO_4
Sulfate ion	SO_4^{2-}
Times	X
Water breakthrough	WBT
Weight percent	wt%

CHAPTER-1: INTRODUCTION

1.1 Thesis structure

The thesis consists of several sections as background, objectives of the thesis, project plan, methodology, results and discussion, conclusion, and recommendations are followed by a reference list. The background part comprises a literature review that includes challenges and perspectives of both surfactant and low salinity water floodings. Initial sections are devoted to the low salinity water flooding and its composition with optimized performance of flooding on complex crude oil, brine, and rock (CBR) interactions. The effect of ionic composition on wettability alteration is highlighted here. Afterward, surfactants are introduced, and the logic behind the choice of the surfactant types for a set of reservoir parameters with complicated CBR is discussed. Special attention is devoted to emphasizing the relevance of low salinity effect on surfactant performance with the help of essential tests as phase behavior and retention analysis.

Thus, as a result, step by step experimentation will lead to the idea that a combination of both methods results in increased oil recovery. Eventually, the proposed hybrid EOR method could be further tested and a project plan for the execution of the laboratory experiments is covered. Namely, the project schedule for implementation of the tasks, resource requirements, and risk management are considered. Then to fulfill designated objectives, laboratory tests are conducted according to the sequence listed in the methodology part. Obtained results are followed by discussion and conclusion sections. Finally, by taking into consideration all points mentioned some recommendations could be suggested for enhanced performance of LSW/LSS in a specific set of reservoir conditions.

1.2 Background

1.2.1 A brief introduction to LSW

The conventional methods in oil recovery are leaving roughly two-thirds of the oil originally in place (OOIP) in the reservoir. Thus, there is a need for approaches to improve oil recovery. A suggested solution is low salinity water flooding (LSW), where brines with reduced dissolved salt concentration are injected into the reservoir instead of the formation brine with the high salinity. Initially, the evolution of this method started from widely applied waterflooding, and then it has been admitted that the injection of decreased salinity made an incremental oil recovery, that revealed the potential of LSW. Also, interest in this method is increasing due to its simplicity and low cost compared to other enhanced oil recovery techniques (Ballah, 2017). In general, the LSW method has been known for decades since the 1960s, but more attention has been achieved only after the 1990s (Tang and Morrow, 1999).

Many studies are confirming the efficiency of LSW. Although most experiments mentioned in the literature relate to sandstones, there is an increasing interest of researchers to apply LSW for carbonates. Moreover, because nearly 60% of the total reservoir shares belong to carbonates, more recent examples of working LSW in carbonates could be mentioned (Yousef et al., 2011). An apparent example of promising results of low salinity waterflooding is the study made by Masalmeh et al. (2019) for carbonate reservoirs during a screening of oil reservoirs in Abu Dhabi. LSW was applied in secondary and tertiary flooding modes, where incremental oil recovery was up to 12.5% and 6.5%, respectively. Also, some studies are correlating experimental data with various models and simulations. For instance, experimental data of LSW on carbonate reservoirs gave 9% more oil recovered compared to the formation water flooding that was in agreement with a proposed model (Wang et al., 2020).

Despite the fact that until 2006 there were less than 3 publications per year devoted to the topic of low salinity waterflooding, there was a rapid increase in the research area that led to the exploration and suggestion of several governing mechanisms by researchers, such as pH variation, fines migration, multi-component ionic exchange (MIE), wettability alteration, double-layer expansion, and interfacial tension reduction (Eikrem, 2014). The process is not fully understood, and the prevailing mechanism is still not identified justifying the need for further studies. The reason for commonly faced wettability alteration behavior has been studied. The proved principal mechanism is a multi-component ionic exchange (Tavassoli et al., 2016).

This governing mechanism can be discussed in more depth. In general, in the case of carbonate minerals, the ions exchange mechanism works as depicted in Figure 1, where a positively charged carbonate surface attracts negatively charged carboxylic parts of oil. To reduce their charge difference and consequently make the weaker attraction of opposite ions, negatively charged sulfates attached to the carbonate surface, and charged oil parts can be displaced with the adhesion of positively charged divalent ions like calcium. As a result, because of electrostatic repulsion, the concentration of Ca^{2+} close to the surface increases and displaces oil particles with carboxylic ends. With elevated temperature (above 70°C), the concentration of ions of SO_4^{2-} and Ca^{2+} correspondingly increases, and ions of Mg^{2+} can replace calcium ions. Moreover, the ion that is essential for wetting preferences of carbonates is sulfate, SO_4^{2-}. Its amount in brine is reduced due to reaction with Ca^{2+} and formation of anhydrate, $CaSO_4$ (s). Thus, the adjustments in the concentration of certain ions as Ca^{2+} and SO_4^{2-} could contribute to the alteration of rock wettability. The term ‘Smart Water’ can be introduced here, which is based on the optimized performance of the oil recovery process with a changed composition of the injected brine. For instance, after altering the amount of the SO_4^{2-} ions from 0 to 4 times concentration of original seawater (SW), it has been identified that oil recovery changed from nearly 10% to 50% of OOIP. Similarly, the concentration of Ca^{2+} ions varied from 0 to 4 times of initial SW that changed oil recovery in the range from 28% to 60% after 30 days of imbibition (Zhang and Austad, 2006, cited in Austad, 2013).

In addition to these ions that take part in wettability alteration, there are some ions such as Na^+ and Cl^-, which are not active in this process, but still limit access to the surfaces and thus should be reduced to optimize ion exchange process. Moreover, the optimization of the oil recovery process with LSW involves not the only reduction of salinity, but also the design of the ions. As a result, the composition of ions should be altered to improve the effect of active ions on CBR interactions in the porous media.

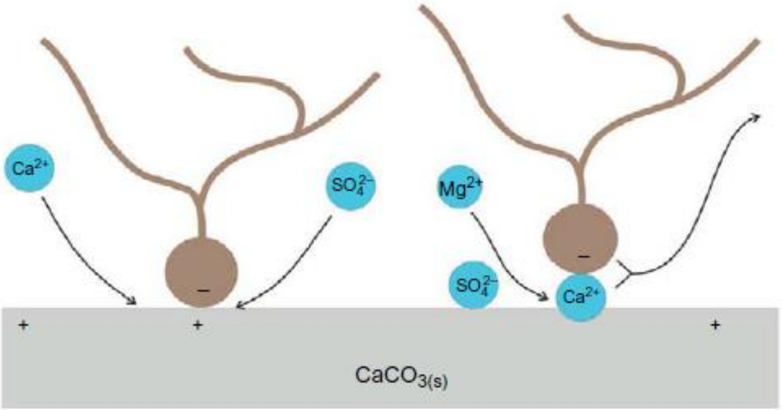


Figure 1. Diagram of the suggested mechanism for carbonate wettability change by SW (Zhang et al., 2007a, cited in Austad, 2013)

1.2.2 A brief introduction to surfactant flooding

Another proven enhanced oil recovery (EOR) technique is surfactant flooding. It comprises the process of mixing a small amount of surfactant in an aqueous solution that injected into the reservoir for extracting more oil. Governing mechanisms are reduced interfacial tension (IFT) between water and oil as well as changing the wettability of reservoir rock surface that has been justified by researchers and field studies (Schlumberger Oilfield Glossary, 2019). As a result, the positive effects of the increased capillary number and enhanced microscopic sweep efficiency lead to a higher recovery factor.

Numerous surfactant flooding studies with promising results exist. For example, in the study carried out by Hashim Abbas et al. (2020) on numerical analysis by CMG-STARS (Computer Modelling Group Company) the benefit of the surfactant flooding is forecasted. Considerable enhancement in oil recovery from 33% to almost 70% was admitted at a continuous injection of anionic surfactant (Aerosol-OT) compared to conventional water flooding. Also, after using continuous surfactant flooding water cut reduced from 95% to nearly 70%. Thus, this surfactant flooding was suitable for heterogeneous Bentiu oil reservoirs.

In the laboratory conditions, the efficiency of a surfactant flood is mainly confirmed by core flooding. Rabbani et al. (2019) conducted tests on tight carbonate (Indiana Limestone) samples to analyze the effect of apparent wettability on surfactant flooding. It was identified that the efficiency of surfactant flooding increases correspondingly with the initial oil-wetness degree of the core samples. Moreover, some researchers analyze experimental results with the help of numerical analysis. For instance, in the study conducted by Saxena et al. (2019), synthesis, characterization, and potential of a new anionic surfactant were investigated. The obtained experimental results were similar with results evaluated from computational fluid dynamics (CFD) analysis. From the fluid-fluid interaction, reduced interfacial tension was 0.01mN/m, also from the fluid-rock interactions wettability alteration towards water wetness of a sandstone core samples was recorded. The enhanced effect of surfactant flooding was confirmed by the coreflooding test with various slug injections. Thus, similarities in the results of experimental and numerical data make findings more valid.

In general, the implementation of a successful EOR project requires screening guidelines. For example, to achieve good performance of surfactant flooding, the selection of the appropriate surfactant and operational parameters are important. Different parameters affect the performance of surfactant flooding. For instance, according to Sheng, (2015), reservoir temperature, oil composition, clay content, and water salinity are critical parameters in surfactant flooding design and implementation. Even though many tests exist to evaluate chemical EOR due to the limited possibilities of laboratory experiments, only three main ones were chosen to screen the surfactant: aqueous stability analysis, the effect of salinity on phase behavior, and oil recovery by coreflooding test (Levitt et al., 2006; Sheng, 2015). As shown in Figure 2, a road map should be followed as the surfactant screening procedure. By this procedure, it is possible to narrow down choices and reach the optimized selection. Initially, compatibility of the surfactant with other components, such as chemical components in the in-situ water is studied. Afterward, to identify the phase behavior of the mixtures, a salinity scan test is implemented, where various test tubes are prepared with altered electrolyte concentration and fixed other parameters. A large middle phase with equal solubilization of oil and water is preferential and defined as optimized salinity (Salager and Antón, 1983). Reduction in IFT at the optimized condition is analyzed at the next step. Possible retention of surfactant on a rock will be measured and analyzed. If the surfactant sample shows an acceptable change in IFT with low retention, then it can be selected for the oil displacement tests. Incremental oil recovery by the selected surfactant is studied by coreflooding experiments. (Sheng, 2015). After completion, all these steps, the appropriate surfactant is screened and selected. The same approach is used in our methodology which will be discussed in more detail in the next chapter.

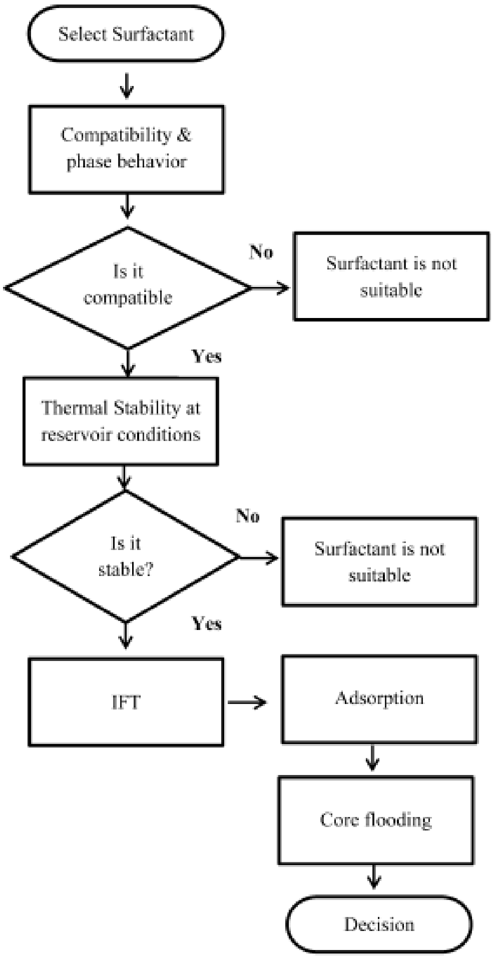


Figure 2.Flowchart of the surfactant screening steps (Kamal et al., 2017)

To achieve the best phase behavior, mixtures of oil, brine, and surfactant samples are prepared and studied to select the best condition, which means the presence of microemulsion phase and low IFT. Three possible environments could be created as a result of interactions of brine, oil, and surfactant. They are lower, middle, and upper phase microemulsion systems that are conventionally called Winsor type II (-), Winsor type III, and Winsor type II (+) from left to right in Figure 3, respectively. In Winsor type II (-), an excess of oil phase exists, and it is assumed that IFT between the water phase and microemulsion is zero due to the solubilization of surfactant in water (Winsor, 1948). Afterward, as salinity is increased, the surfactant moves from the water phase to form a middle phase microemulsion as the desired environment. As a result, optimal salinity is identified from volumes of surfactant, oil, and brine soluble in the middle phase, when an equal amount of solubilization of surfactant in the oil and water phase is reached (Willhite and Green, 1998).

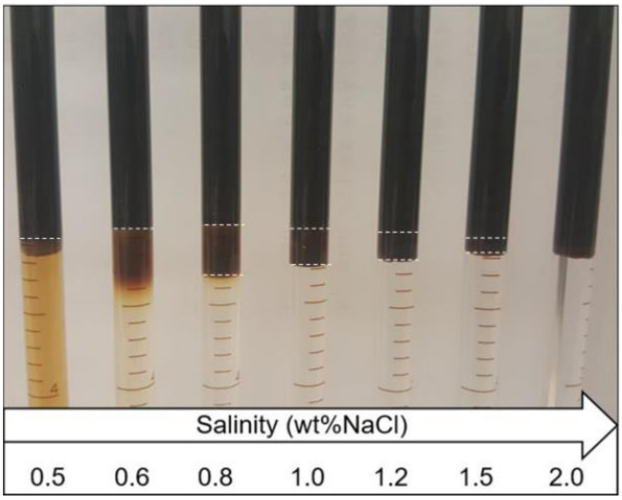


Figure 3. Microemulsion phase behavior as a function of salinity example, where horizontal dashed lines show microemulsion boundaries (Novriansyah et al., 2020)

A similar trend of changes in the solubility with salinity can be seen from the curve presented in Figure 4 below. As a result, the most desired region of middle-phase with reduced IFT and increased solubilization by surfactant of both water and oil phases is achieved and fitted with the help of the addition of different co-surfactants such as alcohols. Thus, for any reservoir, we need to screen surfactants and tailor surfactant/co-surfactant to achieve the best solubilization conditions.

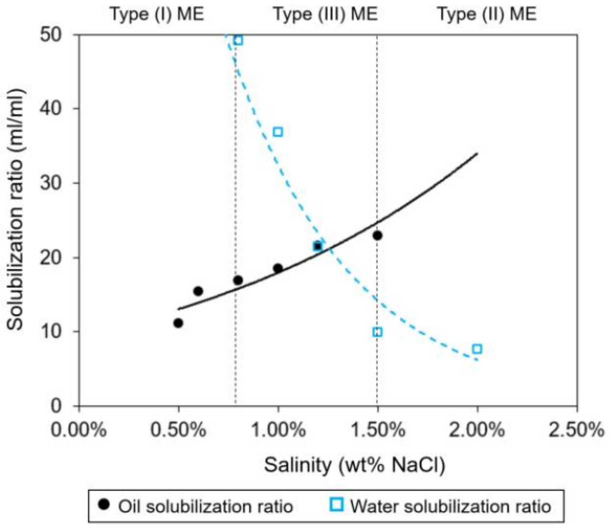


Figure 4. Optimal salinities for solubilization ratio (Novriansyah et al., 2020)

1.3.3 The hybrid LSW/LSS method and its benefits

There is a new trend in development of novel EOR methods to analyze application of hybrid methods. In hybrid methods, different well known EOR methods are combined to achieve benefits of these approaches. Now a new hybrid method could be introduced. The combination of a low saline environment and reduced capillarity by surfactant flooding, called low salinity surfactant flooding (LSS). It is an attractive hybrid method that comprises several governing mechanisms as wettability alteration by low saline waterflooding and reduced interfacial tension from surfactant flooding (Alameri et al., 2015). The benefits of the LSS in terms of higher surfactant stability, low surfactant retention and lower consumption compared to high saline surfactant flooding have been proven (Kamal et al., 2017).

There is a possibility to develop a new hybrid EOR method by consequent injection of LSW and LSS that combines the benefits of both mentioned above. The literature review proves the efficiency of this hybrid LSW/LSS method. The combination of the LSW/LSS method is very effective and results in more than 90% oil recovery after secondary LSW and tertiary LSS flooding (Tavassoli et al., 2016; Dang, 2020). In general, the design of the hybrid method has a typical sequence of injection of LSW followed by LSS. This hybrid method also can be used as a tertiary stage after high saline waterflooding (HSW). Thus, the overall oil production process is optimized, and recovery is increased with HSW preflush to the hybrid LSW/LSS flooding (Morrow and Buckley, 2011).

Similarly, numerous studies confirm promising results of the hybrid LSW/LSS EOR method (Enge, 2014; Endre and Mjøs, 2014; Dang, 2020). To identify this positive effect of the method, coreflooding is a necessary procedure. Thus, there is special attention devoted to the pH and ion composition of the effluent analysis as well as oil recovery and pressure drop profiles within the studied core samples. To identify the impact of each injected fluid, different sequences are implemented. For example, as presented in the study by Alagic and Skauge, (2010) and illustrated in the diagram in Figure 5, injection to four Berea sandstone cores after aging in crude oil have been considered. The first two cores, B1 and B2, were used for LSW, which had 5000 ppm NaCl and afterward subjected to LSS; with the same salinity 1.0 wt % of internal olefin sulfonate Enordet 0242L by Shell Chemicals and 1.0 wt % isoamyl alcohol (IAA).

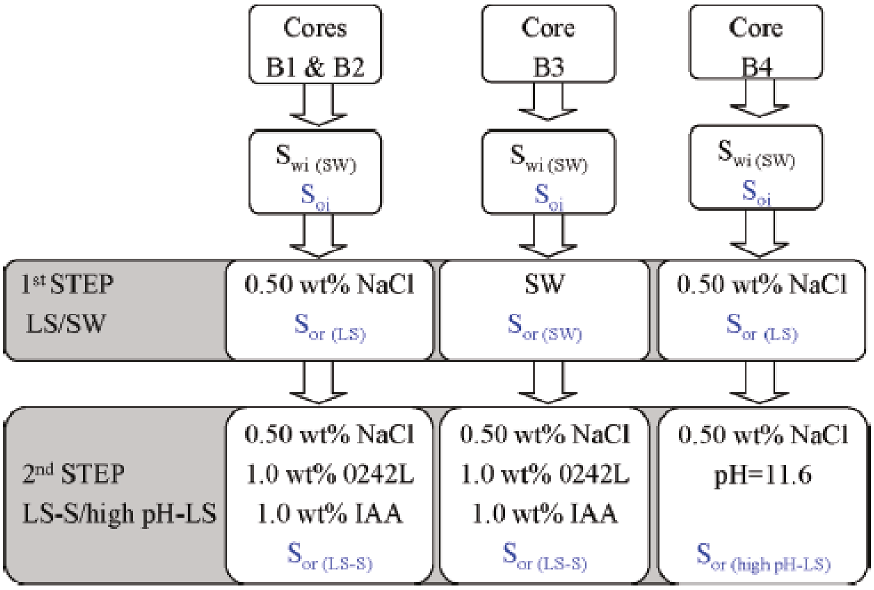


Figure 5. Flowchart with an experimental procedure for coreflooding (Alagic and Skauge, 2010)

As a result, obtained oil recovery for these cores ranged from 92% to 94% of OOIP as can be seen in Figure 6. While for core B3 that underwent injection of seawater (SW), with higher salinity, in secondary mode and LSS in tertiary mode oil recovery was 45%. Hence, without preflush with low saline brine, surfactant performance to recover oil was weaker. This proves the benefit of the hybrid method application.

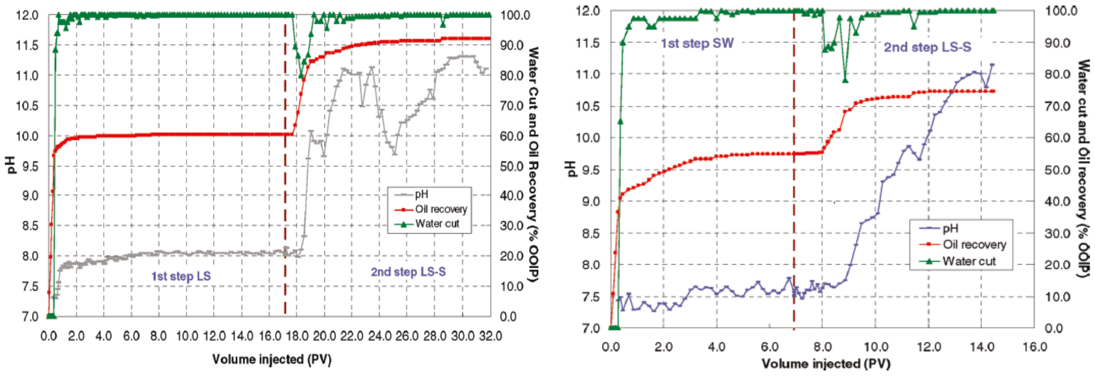


Figure 6. At discharge pH, oil recovery, and water cut versus pore volume (PV) injected for core samples B1 and B3 from left to right, respectively (Alagic and Skauge, 2010)

In general, advances proposed by the hybrid LSW/LSS method can be even seen from the capillary desaturation curve (CDC). The combined effect gives practically better results rather than predicted values by the CDC that is an essential parameter characterizing the connection between capillary pressure and residual oil saturation. Similarly, this relation can be seen from the experiments conducted by Johannessen and Spildo (2013) on relatively different two sets of Berea core samples with absolute permeability, Kw, equal to 100 md (designated heterogeneous) and equal to 300 md (designated as homogeneous). Recorded residual oil saturations for two sets of cores were 0.37 and 0.25 with reduced IFT to 0.02 mN/m after tertiary injection of surfactant flooding at low salinity; these experiments showed higher oil recovery than values predicted by CDC curve on Berea sandstone cores. A similar conclusion was obtained from the study of Spildo et al., (2012), where dampened effect after LSS is attributed to the redistributed oil because of complex crude oil/brine/rock (CBR) interactions affected by preflush with LSW. It means that the instability of oil layers by altered wettability from oil-wet to water (or mixed wet) condition by LSW makes the performance of LSS better with higher oil recovery (Derikvand et al., 2020). Thus, the combined implementation of the hybrid method results in lower residual oil saturation than for the predicted values by only surfactant flooding.

Mostly in the literature, the hybrid LSW/LSS method was applied with sandstone core samples. However, there are some recent studies of the hybrid method with promising results in the carbonate formations as well. For example, in the study conducted by Alameri et al., (2015) the benefit of the hybrid LSW/LSS method was justified by wettability alteration of the initially oil-wet carbonate surface towards a water-wet condition and reduced interfacial tension between oil and water phases. Finally, the potential of the combined method was analyzed in terms of the coreflooding test. Here sequential injection of seawater followed by LSW recovered 57%, while tertiary injection of LSS recovered an additional 10%. In the study, the effect of reduced salinity by dilutions from 2 to 50 times of seawater has been analyzed. The most optimized one was four times diluted seawater (12840 ppm) that was then used with a surfactant as tertiary injection fluid (Alameri et al., 2015) However, there are some updates in the recent researches with adjustments of the ionic composition of the brines, when the term of smart water is incorporated into LSW/LSS hybrid method. For example, in the study by Dabiri and Honarvar, (2020) on oil-wet carbonates, the synergy of the surfactant in low saline brine with optimized ionic composition was analyzed. In terms of wettability alteration, it changed contact angle from 134.82° to 36.98°, from oil-wet to water-wet condition, respectively. Also, the benefit of the hybrid method was checked in the coreflooding test. The recovery factor in the sequential injection of LSW was 71.46 % and it increased up to 84% after tertiary LSS injection. Thus, from the abovementioned literature, it could be deduced that enhanced oil recovery factors are depicting a potential of the hybrid method in both sandstone and carbonate samples.

Minimized surfactant retention is another essential benefit of the hybrid method that affects the economic feasibility of the project. The retention was measured to be 10 times lower for the case of LSS compared to the higher saline optimum salinity seawater (OSS) flooding (Spildo, 2014). It can also be calculated from the data presented in Figure 7, where a vertical axis depicting the ratio of effluent to influent concentration and a horizontal axis corresponding to the injected pore volume (PV). Thus, the smaller area under the curve assigned to the higher value of retention of the surfactant and it can be seen from the given Figure 7 that OSS has a lower area under the curve with correspondingly higher retention value. The reason behind increased retention is because of the increased calcium ions in the higher salinity, which in turn inversely affects surfactant adsorption (Khanamiri et.al, 2016). Thus, increased adsorption of chemicals on the rock results in more retardation and excess expense that confirms optimized usage of surfactants in the hybrid method. Also, the low saline environment allows a chance for more available surfactant choices without a need to tailor as in the case of high salinity water flooding to achieve ultralow IFT (low) that makes the process more convenient and cheaper (Alagic and Skauge, 2010; Spildo et al., 2014).

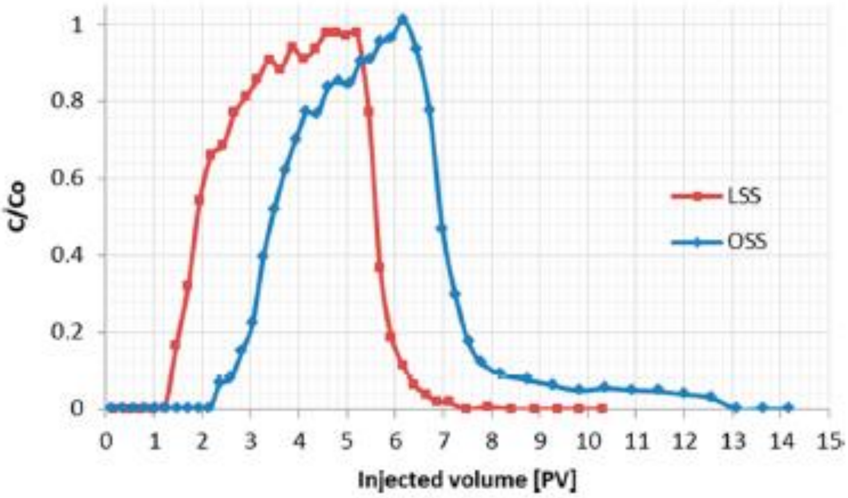


Figure 7. The ratio of effluent to the influent concentration of surfactant versus injected pore volume for retention profile (Johannessen and Spildo, 2013)

Another essential point to highlight is that the application of the hybrid method and combining LSW and surfactant flooding improve the performance of both methods. Positive results can be explained by the compatibility of methods, where a favorable environment for surfactant is created by low saline water. For example, such performance criteria for surfactant behavior are distinguished by improved solubility as well as a reduced loss of concentration of the chemical (Bera et al., 2014). For example, by the hybrid method at low salinity, it is possible to achieve high oil recovery even not at ultra-low IFT as shown by Johannessen and Spildo (2013).

Flooding at two salinity conditions was analyzed, one the optimum case, where surfactant creates the ultra-low IFT condition, here seawater diluted by multiple of 0.43, and low salinity conditions, where the water was diluted by a factor of 0.07. Although for the case of ultralow IFT at optimum salinity there are 2 orders of magnitude higher capillary number compared to the low salinity case, there are similar results of oil recovery obtained. Therefore, it might be suggested that besides the reduced IFT, the wettability alteration mechanism due to LSW is also effective. In other words, comparable results achieved by the LSS with optimum salinity surfactant (OSS) are leading to the idea of several governing mechanisms in increasing oil recovery in the hybrid LSW/LSS method as wettability alteration and IFT reduction. Hence, it confirms the benefit of the hybrid method (Johannessen and Spildo, 2013).

There is a need to further study to separate effects of ion composition not only on oil recovery provided by the hybrid method but also on essential parameters such as IFT and critical micelle concentration (CMC). For instance, from the experiments conducted by Khanamiri et.al, (2016) on Berea core samples, it has been concluded that combination of an increased ratio of divalent ions concentration to monovalent ions concentration (Ca^{2+}+ Mg^{2+})/ Na^{+} (equal to 0.033) with an injection of pure sodium chloride results in higher oil recovery. Moreover, the change ratio of divalent to monovalent from 0 to 0.033 results in lower CMC that enhances the LSW/LSS hybrid method by making the process beneficial. Critical micelle concentration at different ionic strengths in the presence and absence of Ca^{2+} changed from 105 mg/L to 65 mg/L after the addition of Ca^{2+}/Na^{+} at a ratio of 0.022 to the solution with the same ionic strength. Thus, the role of calcium is more important, especially in surfactant flooding, and it has a positive effect on the stabilizing of micelles. Thus, CMC is essential in correlating IFT between oil and surfactant solution. For example, the general trend of reduced

IFT value corresponding to increased Ca^{2+} ion concentration recorded by the spinning drop tensiometer can be confirmed by Figure 8.

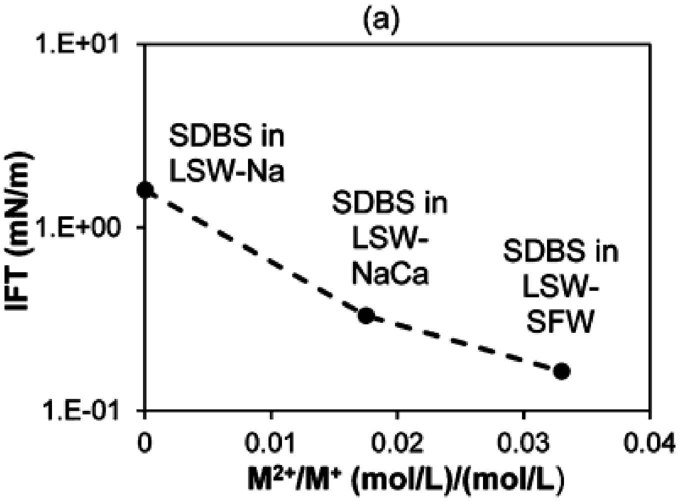


Figure 8. IFT of crude oil with 500 mg/L of anionic surfactant at different divalent to monovalent molar ratio, (Khanamiri et.al, 2016)

There is a similar study by Mohammadi et al. (2019) on carbonate rocks, where the effects of Mg^{2+}, Ca^{2+}, and SO_4^{2-} ions on the performance of oil expulsion were studied. As a result, impact of SO_4^{2-} ion was hindered at the presence of surfactant. Meanwhile, the presence of divalent ions was identified to be effective in the reduction of IFT. However, excess of Ca^{2+} ions was considered as disturbing ions. Therefore, the application of LSW/LSS is more favorable at conditions with an optimized amount of divalent calcium ions, without excess amount that can affect the performance of the surfactant adversely and lead to aggregation of chemicals (Mohammadi et al., 2019).

1.3.4 Parameters affecting the performance of the LSW/LSS hybrid method

There are essential factors that influence the overall performance of the LSW/LSS hybrid method. An important parameter that is considered as a significant prerequisite for successful LSW and LSS coreflooding is the initial wettability condition. For instance, there is a study devoted to the aging effect on LSW/LSS flooding by Alagic et al. (2011), where two Berea sandstone cores were not aged and tested at natural state, while other two were aged in the crude oil at elevated temperature. Thus, from the obtained results of analyzing coreflooding tests, there is a higher recovery by LSW/LSS hybrid method in the aged core samples. Besides, wettability alteration to more water-wet core samples can be qualitatively confirmed by the oil production curve shape during LSW/LSS that is illustrated in Figure 6. In the oil production profile, a plateau is reached faster, and there is no long tail production after water breakthrough (WBT) with the higher oil recovery, which is an evidence of a water-wet system compared to high salinity, SW flooding cases corresponding to the more oil-wet system. Quantitatively it can be tested as well via contact angle measurement for identification of the rock surface wetness at different stages of brine salinity or surfactant treatment (Teklu et al., 2017).

It has been identified by some researches that there is no incremental oil recovery for LSW without a water wet initial condition, as in the case of Eikrem, (2014), where additional oil recovery by LSW was nearly 3-5% of OOIP for aged core samples, and no response to LSW was observed without aging on the similar sandstone samples. Also, LSS indicated a difference in OOIP from 60% to roughly 75% in the aged core samples after treating core with LSW and afterward with LSS. Hence, the hybrid method works better in oil-wet systems, where the injection of LSW/LSS is more effective to change the wettability to the water-wet condition. Thus, in the laboratory scale to have the significant effect of LSW/LSS, the role of wettability alteration is immense. For both LSW and LSW/LSS conditions, less-water wet core distinguished by more destabilized oil layers with a higher amount of continuous oil leads to higher oil recovery (Karimi et al., 2016).

There is a different study made on Berea sandstone cores aimed to identify the influence of five various brine compositions of NaCl, $CaCl_2$, and $MgCl_2$ on LSW and LSS performance. Coreflooding experiments were conducted on nine aged core samples. In general, the procedure for laboratory studies was mostly coinciding with each other that encounter the following steps; as the first core was drained by high saline water until achieving initial water saturation, Swi, and then it was flooded by the hybrid LSW/LSS. As a result, it can be deduced from the data that the best performance of LSS was by the brine composition of 9% NaCl, 0.9% $CaCl_2$ and 0.1% $MgCl_2$ used for both saturation and coreflooding where additional incremental oil recovery of 9.3% of OOIP was achieved (Araz, 2014). Almost the same investigation was implemented by Enge (2014), where cores were flooded by LSW in secondary mode and by the anionic surfactant, Sodium Dodecylbenzene Sulfonate (SDBS), solution at low salinity in a tertiary mode both at an operating temperature of 60^o C. It concluded that the most significant contrast between in-situ and injected brines divalent ion compositions leads to the highest oil recovery. As a result of stripped divalent ions from the rock surface after pure NaCl flooding water-wetness was promoted. Thus, oil recovery after secondary LSW was in the range of 42.3-57.7% and after tertiary LSS incremental oil recovery was 2.1-8.8% of OOIP. Similarly, from the study conducted by Aminian & Zarenezhad, (2019) on carbonate and sandstone rock samples, it was deduced that the presence of divalent ions in the formation water promoted oil wetness of the rock surface. Also, the performance of LSS was better in case of a small increase in the Ca^{2+} ions that was mainly due to an increase in interfacial elasticity. The reason was behind compact structures of the surfactant in the presence of divalent ions. Therefore, from these studies, it could be admitted that the chemistry and composition of the injected brine has a significant effect on the performance of the LSW/LSS method, and it is required to optimize the composition of the smart water to enhance oil extraction process (Enge, 2014).

1.3.5 Related developments to the hybrid LSW/LSS method

Except for factors related to higher oil recovery of the project, there are some factors concerning environmental issues. Therefore, there is an increasing interest in the biodegradable surfactants produced from renewable natural resources like plant oil (e.g., palm oil). Moreover, due to the increased interest in the hybrid method of LSW/LSS, there is an intensive investigation in the direction of more eco-friendly alternatives to the proposed projects (Ahmadi and Shadizadeh, 2012). For instance, a study made by Moradi et al., (2019) on carbonates, where a new natural surfactant, Tribulus Terrestris, has been used for the hybrid method. Even though nonionic (natural) surfactants are not as effective in reducing IFT as ionic ones, there is compensation by LSW with an altered ionic composition (smart water). There is enhanced oil recovery from 45.2% to 71.8% for distilled water and the hybrid method, respectively. Thus, from this paper, it can be deduced that combined LSW/LSS method was showing promising results in the laboratory scale even with a nonionic biodegradable surfactant that changed IFT insignificantly from 45.3 mN/m to 13.5 mN/m at CMC of 0.3 % (at the same time, less adsorption by nonionic should be taken into consideration). The overall performance of the hybrid method was successful. Therefore, there are possible ways of the LSW/LSS method development in the direction of simultaneous consideration of environmental aspects with the profitability of the project with higher oil recovery.

For carbonate formations, commonly cationic or non-ionic surfactants are preferred. The reason is behind positively charged carbonate surface that is supposed to have higher adsorption of anionic surfactants due to electrostatic attraction. However, there are some studies confirming a relatively equal amount of adsorption plateaus of some cationic and anionic surfactants (Ma et. al., 2013). For example, in the study by Rosen and Li (2001) adsorption plateaus of cationic surfactant decyltrimethylammonium bromide ($C_{12}TAB$) and anionic surfactant disodium didecyldiphenylether (DADS) were $5.7*10^{-7}$ mol/g and $5.12*10^{-7}$ mol/g, respectively. Also, Chen and Mohanty (2013) investigated the wettability alteration effect on oil-wet carbonate cores by anionic and cationic surfactants. At high temperature and high salinity cationic surfactants altered wettability towards the water-wet condition and recovered up to 65% of OOIP from spontaneous imbibition test, while anionic one changed wettability to strongly water-wet condition only in the case of the reduced brine salinity. The addition of alkalis to the anionic surfactant formulation as ethylene diamine tetraacetic acid (EDTA) and sodium carbonate (Na_2CO_3) showed benefits in terms of wettability alteration, reduced adsorption of surfactants to the carbonate surface and assist saponification. Moreover, anionic surfactants are more capable of achieving ultralow IFT between oil and water phases and less expensive (Chen and Mohanty, 2013; Kamal et al., 2017). Thus, in the current thesis, it is preferred to work with anionic surfactants.

The addition of polymers can further develop a modification of the studied hybrid method of low salinity water and surfactant flooding. It is commonly used to control the mobility of the injected fluid and maintain the stability of the front (Pourafshary and Moradpour, 2019). Thus, this hybrid EOR method is called surfactant-polymer (SP), which respectively improves microscopic and macroscopic sweep efficiencies. Similarly, as for solely surfactant flooding at LSW, SP leads to higher oil recovery at reduced salinity as well. Supporting data can be extracted from the publications by Wang et al. (2018), where SP at LSW performs higher oil recovery to more than 5% of OOIP than at high saline case.

Moreover, results obtained by the experimental procedure can be confirmed by the simulation encountering the multi-mechanistic modeling approach presented by Tavassoli et al., (2016). The UTCHEM-IPhreeqc simulator involves various data from geochemistry, surfactant phase behavior, reaction kinetics, interfacial tension, front stability, and other complex parameters that are essential for evolving accurate models. They concluded that there are two effective mechanisms involved in the hybrid method, which are wettability alteration corresponding to low salinity water flooding and interfacial tension reduction by low salinity surfactant flooding. Similarly, a study on modeling and experimental results comparison was made by Khaledialidusti et al., (2017) on LSS/LSW hybrid method. For example, cumulative production data versus time graph of the study is depicted in Figure 9 below, where red points corresponding to experimental data and the derived model trend line are almost fitted to the practical data. However, it should be noted that the modeling impact of surfactant flooding on wettability is neglected.

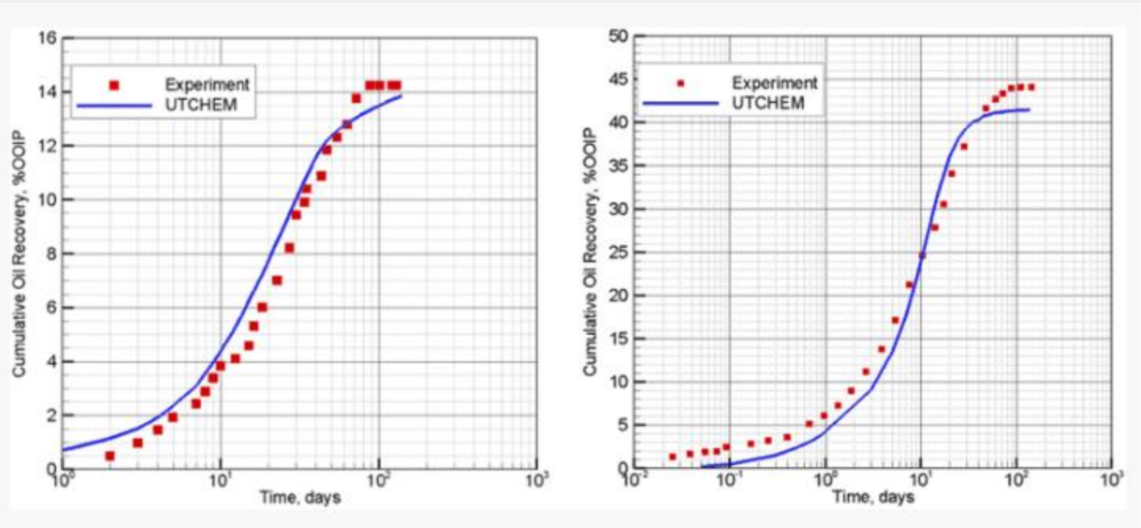


Figure 9. Comparison of simulated and experiment imbibition cell test for different cases (Khaledialidusti et al., 2017)

Although simulation indicating a slower pace of obtaining the desired output, at the end of complicated iterative estimations, experimental results and data from the simulator are coinciding with the same oil recovery, pressure gradient profile and ionic composition of the effluent brine (Tavassoli et al.,2016). Thus, models proposed for LSW/LSS system are working appropriately.

1.3 Problem definition

The conventional oil recovery techniques are leaving about two-thirds of oil originally in place in the reservoir. Thus, there is a need for approaches to improve oil recovery methods. A suggested solution is a combination of LSW and LSS. Despite some challenges associated with separate methods; they can be overcome in combination. For example, there is a lack of availability of surfactants working at high salinity. Moreover, despite questions left about the governing mechanism of LSW, the presence of the preflush of LSW before surfactant flooding creates favorable conditions for the latter one.

Based on the abovementioned literature studies another difficulty is related to a small number of already existed studies of carbonate formations with a hybrid LSW/LSS method. It makes the development of a methodology more difficult. However, this challenge encourages us to create a specific screening procedure of the current thesis that could be then justified by the coreflooding test at the end of experiments.

Also, it could be admitted that previously in the hybrid LSW/LSS method mainly effect of the only dilution has been discussed, not the effect of smart water with the optimized ionic composition of diluted brines. The missing points in other studies making the current study more relevant with the possibility to propose a new design for the LSW/LSS system.

Moreover, the electrostatic attraction of positively charged carbonate surface and negatively charged anionic surfactant makes the application of anionic surfactant with carbonates challenging. As a result, commonly studies are based on cationic or non-ionic surfactants for carbonate formations. However, there are some benefits of the anionic surfactants as lower price, effectiveness in reducing IFT, stability to salinity and temperature, while adsorption problem could be solved by some sequestration alkalis.

To sum up, based on the already existed challenges listed in literature a new LSW/LSS hybrid method suitable for Kazakhstani oil fields could be developed in the current thesis. It has a few features compared to already existed studies that are going to be discussed in further chapters.

1.4 Objectives of the thesis

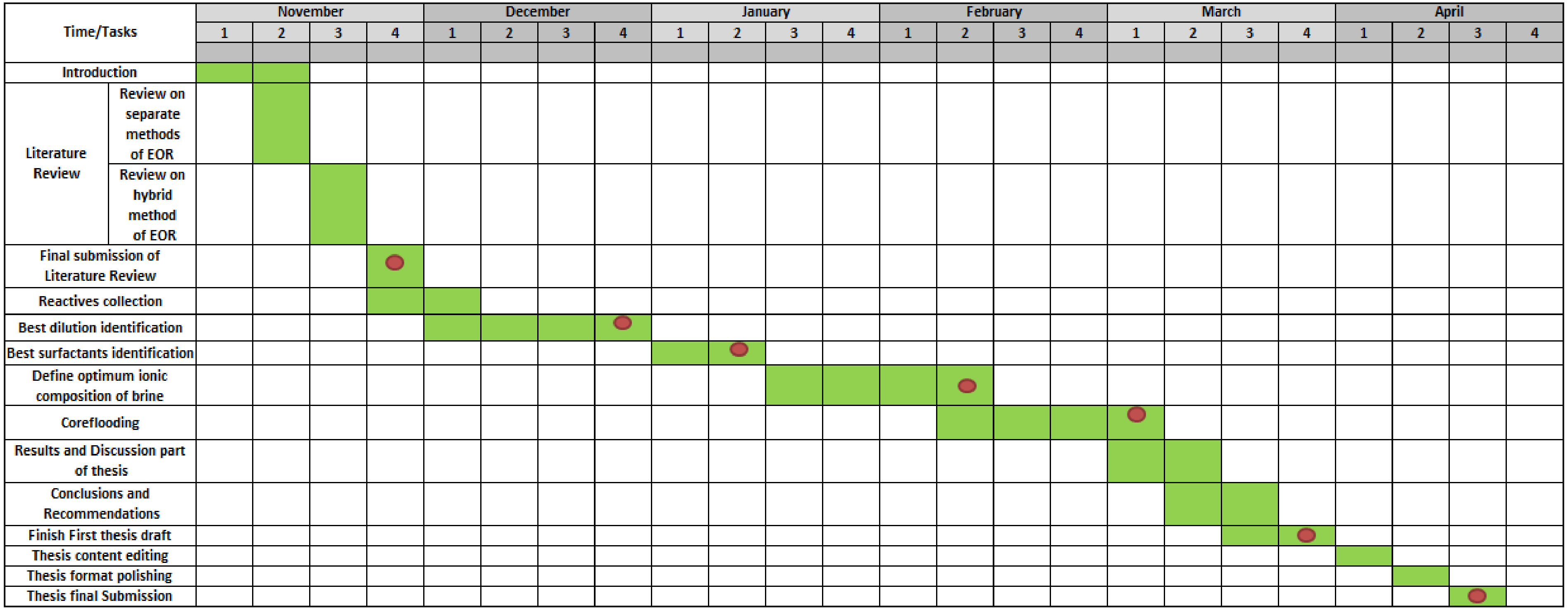
1.4.1 Main objectives

The objective of this thesis is to design an LSW/LSS hybrid method for carbonate formations with the optimized performance of ‘Smart Water’ due to enhanced wettability alteration towards the more water-wet system. Also, to use these specific salinities to screen the most appropriate surfactant types that in combination will lead to higher oil recovery. Screening conditions here are corresponding Kazakhstani oil fields. To achieve the designated objective there are some tasks, such as the development of a methodology for screening. Its efficiency could be evaluated from the incremental oil recovery by the coreflooding test and the overall benefits of the hybrid LSW/LSS method are going to be studied.

CHAPTER-2: PROJECT PLAN

1.1 Project schedule

Below Gannt Chart is presented. It was developed to ensure that the project will be delivered on time.



Time/Tasks		November				December				January				February				March				April			
		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Introduction		🟩	🟩																						
Literature Review	Review on separate methods of EOR		🟩																						
	Review on hybrid method of EOR			🟩																					
Final submission of Literature Review					🟩●																				
Reactives collection					🟩	🟩																			
Best dilution identification						🟩	🟩	🟩	🟩●																
Best surfactants identification										🟩	🟩●														
Define optimum ionic composition of brine												🟩	🟩	🟩	🟩●										
Coreflooding															🟩	🟩	🟩	🟩●							
Results and Discussion part of thesis																		🟩	🟩						
Conclusions and Recommendations																			🟩	🟩					
Finish First thesis draft																				🟩	🟩●				
Thesis content editing																						🟩			
Thesis format polishing																							🟩		
Thesis final Submission																								🟩●	

Figure 10. Thesis schedule

● - milestones

1.2 Resource requirements

The necessary resources for project completion are identified and listed.

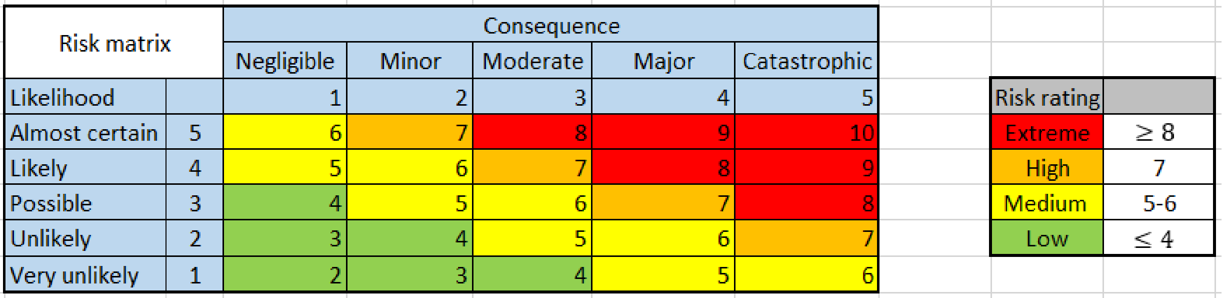
Table 1. Required resources

Device/material	Function
Laptop	To convey materials for research into written form
The equipment listed in the methodology part	To perform experiments such as contact angle measurement, phase behavior, and coreflooding
Printer	To print out materials
Access to the internet	To download essential information related to the thesis

1.3 Risk management

Some risks are related to the current thesis. They could be obstacles in achieving assigned objectives and as a result, reaching the desired outcome would be problematic. Therefore, a well-planned risk management strategy is required. For instance, WRAC analysis could be considered that is a common risk assessment tool. It uses a 5x5 likelihood-consequence matrix. Namely, risks are classified from low to an extreme case that is depicted in Table 2.

Table 2. 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

1.3.1 *Physical hazards*

A physical hazard is a circumstance that could cause harm without the need for physical contact. The possible physical hazards that can occur during the thesis work and the ways of avoiding them are given in Table 3.

Table 3. Physical hazards

Physical Hazard	Description	Risk rating	Risk Control
Eyestrain or irritation	Irritation from prolonged presence in front of the computer screen or effect of chemicals in the laboratory	7 High	Exercises for eyes, breaks during usage of computer and laboratory work that is accompanied by regular ventilation of workspace; safety rules of the lab have to be followed with safety glasses and gloves constant usage
Skin corrosion/irritation	Damage from the contact with various chemicals in the laboratory (e.g., surfactants, salts, crude oil, etc.)	7 High	Follow safety regulations of the lab area with constant usage of safety gloves, a lab coat, and other protective clothes. Wash face, hands and any exposed skin thoroughly after handling
Irritation in nose or throat (airways hazard)	Inhalation of hazardous chemicals or vapors in the laboratory	7 High	Ventilate well working areas, avoid breathing vapors. Use approved respirator if air contamination is above the accepted level.
Fire and explosion hazards	Some materials release flammable vapors at or below ambient temperatures (crude oil). When mixed with air in certain proportions and exposed to an ignition source, these vapors can burn in the open or explode in confined spaces.	7 High	Treat with special precautions work with materials under a fume hood to avoid hazardous vapors in a well-ventilated location. Keep away from heat, sparks, and open flame. Keep containers closed, plainly labeled and out of closed vehicles.
Burns under high temperature	To reestablish reservoir condition oven and core aging cylinders heated with mantles are used	7 High	Safety measures in the laboratory have to be followed especially during work at elevated temperature; special thermally resistive gloves usage is obligatory
High-pressure hazard	To reestablish reservoir condition core aging cylinders under high pressure are used	7 High	Safety measures in the laboratory have to be followed especially during work at high pressure with constant control of the process; functionality of all types of equipment have to be checked in advance of launching an experiment with constantly recording values from pressure sensors and in case release valve could be used
High stress	Stress from the overwork	5 Medium	Proper time management, meditation, breaks during work
Illness	Disease from mild colds to flu	5 Medium	Maintain immunity, dress warmly

1.3.2 Project hazard

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

Table 4. Project hazards

Project hazard	Description	Risk level / rating	Risk control
Thesis related documents loss	Sudden failure of the hard drive, computer crash due to viruses, not saving the thesis files	3 Low	Use cloud services like google drive, do not forget to save, installation of anti-virus software
Absence or failure of equipment for experiments	Equipment might break and be out of service for continuation of experiments	5 Medium	Equipment under guarantee and in case of any malfunctions producers have to be informed and it is going to be fixed; also, some reserve tests or correlations instead of certain experiments could be conducted; supervisors have to be informed at each stage of the project
Lack of consumables and chemicals	Some chemicals are ended up faster than expected or there is no required chemical at all	5 Medium	Laboratory technicians have to be informed in advance about required consumables; in case of delayed delivery some chemicals could be replaced with others and supervisors have to be informed at each stage of the project

CHAPTER-3: METHODOLOGY

3.1 Materials

3.1.1. Crude Oil

To fulfill the designated objective of the thesis and apply findings of the study in Kazakhstani oilfields, local raw materials have been preferred. Therefore, crude oil from West Kazakhstan (Aktobe region) was used, and its composition is indicated in Table 5.

Table 5. Crude oil composition

Component	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15+	other
Wt%	0.8	0.43	1.63	7.36	8.7	17.87	5.09	5.44	8.3	6.15	30.55	7.66

Other basic parameters of the crude oil as viscosity and density have been recorded with help of SVM 3001 Viscometer from Anton Paar. They were measured at three different temperatures of 20°C, 50°C, and 80°C; these results are illustrated in Figure 11.

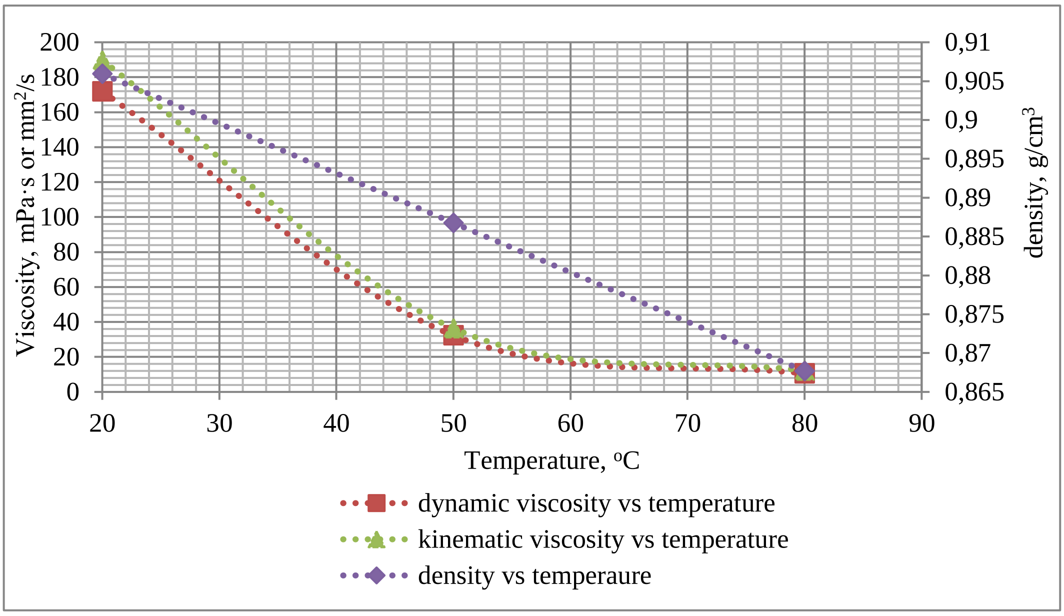


Figure 11. Crude oil basic parameters as dynamic, kinematic viscosity and density versus temperature

3.1.2. Rock type (porous media)

In this study, carbonate outcrops were used. Namely, core plugs of limestone family were chosen, and pellets were prepared from them. They have been divided into same pellets 1-inch lengths; 1.5 inches diameter half circles with roughly smooth surfaces as it is depicted in Figure 12. On these flat surfaces, contact angle measurement tests carried out on both sides. Moreover, from X-ray Diffraction (XRD) analysis made on the core sample, it was identified that material mainly consists of calcite (about 99%).

Figure 12. Core samples

3.1.3 Aqueous solution

There are certain salt types used for brine preparation by considering their purity that is listed in Table 6.

Table 6. Required chemicals for different brine preparation

Required chemicals	**Chemical formula**	**Purity**	**Producers**
Sodium bicarbonate	$NaHCO_3$	≥99.0%	SIGMA-ALDRICH
Sodium sulfate	Na_2SO_4	≥99.0%	
Sodium chloride	NaCl	≥99.0%	
Calcium chloride dihydrate	$CaCl_2.2H_2O$	≥96.0%	ACROS ORGANICS
Magnesium chloride hexahydrate	$MgCl_2.6H_2O$	≥99.0%	SIGMA-ALDRICH

High Salinity Water (HSW) that was synthetic formation water was used to achieve the initial condition of the core samples. The composition of HSW is from an oil field in West Kazakhstan (Tengiz) that is nearly 180 ppm and its composition is presented in Table 7.

Table 7.Composition of major ions of formation water in the Tengiz oil field (Isabaev Y. et. al., 2015)

Ions	Formation water, ppm
Na+ + K+	81600
Ca^{2+}	9540
Mg^{2+}	1470
Cl^{-}	90370
Total	181980

Afterward, the South Caspian Sea from the Western part of Kazakhstan has been chosen as a base brine for waterflooding that has a salinity of 13 000 mg/L. To conduct low salinity water flooding, different samples of diluted brine were prepared as shown in Table 8. The base water was diluted for 2, 10, and 20 times to study the effect of dilution on the performance of waterflooding.

Table 8. Ionic composition of dilutions

Ions	South Caspian Sea (SW), ppm	2 times dilution, ppm	10 times dilution, ppm	20 times dilution, ppm
$Na^{+} + K^{+}$	3240	1620	324	162
Ca^{2+}	350	175	35	17,5
Mg^{2+}	740	370	74	37
Cl^{-}	5440	2720	544	272
SO_4^{2-}	3010	1505	301	150,5
HCO_3^{-}	220	110	22	11
Total	13000	6500	1300	650

As we mentioned before, the performance of LSW to alter oil/brine/rock interactions can be enhanced by adjusting active ions in the water composition. Hence, different types of "Smart Water" were prepared by adjusting the concentration of active ions which are SO_4^{2-}, $Ca^{2+}$and Mg^{2+}.

Sulfate ions are playing a catalytic role in displacing the carboxylic group from carbonate surfaces by divalent ions like magnesium and calcium ions. Moreover, some researchers admitted that seawater containing two times higher concentration of sulfate ions than divalent calcium ion could be excellent wettability alternating reference fluid (Strand et al., 2006; Zhang and Austad, 2006). Therefore, in the considered brine samples composition of sulfate ions are two times higher than calcium and magnesium ions to enhance the effect of studied fluids to alter wettability.

In the current study impact of ionic groups has been investigated. Hence, samples were prepared and concentrations of $Mg+SO_4$, $Ca+ SO_4$ and $Mg+Ca+SO_4$ were spiked. To trace the effect of magnesium and sulfate group or calcium and sulfate group, the concentration of both calcium and magnesium increased for two, three and four times, while the concentration of sulfate ions was spiked twice more than divalent cations. In this research, a specific format is used to clarify the type of water. For example, 10SW, 4S, 2Mg, 2Ca shows 10 times diluted Caspian Seawater in which the concentration of sulfate ions is spiked for four times and concentration of calcium and magnesium cations are increased twice.

Table 9 shows the composition of different smart water samples prepared for this study. The effect of each sample on the interaction between fluids and rock was studied and compared together to achieve the most effective brine for a successful smart water flooding operation.

Table 9. Composition of ions in each sample (1-8)

Ions	10SW-S, Mg, Ca	10SW-0S, Mg, Ca	10SW-4S, 2Mg, 2Ca	10SW-4S, 2Mg, Ca	10SW-4S, Mg, 2Ca	10SW-6S, 3Mg, Ca	10SW-6S, Mg, 3Ca	10SW-8S, 4Mg, 4Ca
Na^+ + K^+	325	325	325	325	325	325	325	325
Ca^{2+}	35	35	35	35	70	35	105	140
Mg^{2+}	74	74	74	148	74	222	74	296
Cl^-	544	544	544	544	544	544	544	544
SO_4^{2-}	301	0	602	1204	1204	1806	1806	2408
HCO_3^-	22	22	22	22	22	22	22	22
Total	1301	1000	1602	2278	2239	2954	2876	3735

Solutions could be prepared by using the following recipes depicted in Table 10 below, where the composition of ions altered.

Table 10. Recipes for the altered ionic composition of SO_4^{2-}, $Ca^{2+}$and Mg^{2+} ions

Sample fluid number	1	2	3	4	5	6	7	8
mg per 0.5 L	10SW-S, Mg, Ca	10SW-0S, Mg, Ca	10SW-4S, 2Mg, 2Ca	10SW-4S, 2Mg, Ca	10SW-4S, Mg, 2Ca	10SW-6S, 3Mg, Ca	10SW-6S, Mg, 3Ca	10SW-8S, 4Mg, 4Ca
Na_2SO_4	0.22	0	0.89	0.89	0.89	1.34	1.34	1.78
NaCl	0.23	0.41	0	0	0	0	0	0
$CaCl_2.2H_2O$	0.06	0.06	0.06	0.06	0.13	0.06	0.19	0.26
$MgCl_2.6H_2O$	0.31	0.31	0.62	0.62	0.31	0.93	0.31	1.24

3.1.4. Surfactant

In the current work, it is preferred to work with anionic surfactants. This type of surfactant is more capable of achieving ultralow IFT between oil and water phases and cheaper. Moreover, the challenge related to surfactant adsorption to the carbonate surfaces could be fixed by adding alkali (Na_2CO_3) and changing the surface charge of carbonate to a negative one (Chen and Mohanty, 2013).

In this study, four types of surfactants were utilized for experimental work. We used two surfactants of benzenesulfonic acid, dimethyl-, mono-C11-16- alkyl deriv. (XOF-25S) and benzenesulfonic acid, C14-24-branched and linear, alkyl deriv. (XOF-26S) that supposed to be thermally stable at 80°C from Huntsman. These are alkyl aryl sulfonate. They interact very well with crude oils with short hydrocarbon lengths. Also, we used two types of anionic surfactants of benzenesulfonic acid, 4-C15-16-sec- alkyl deriv. (Soloterra 117H) and benzenesulfonic acid, 4-C10-13-sec- alkyl deriv. (Soloterra 113H) that have been provided by Sasol Company. Similarly, they supposed to be stable at 80°C and commonly used in achieving low IFT.

The co-surfactant of oxirane, methyl-, polymer with oxirane, mono (2,4-dinonylphenyl) ether (XOF-314C) from Huntsman was used as well. It is suggested by producers to mix this co-surfactant with the main surfactant in a 50:50 to 30:70 ratio. Because of the hydrophobic and hydrophilic parts of surfactants that interact with crude oil and brine respectively, IFT between oil and brine interfaces reduces. Thus, such combinations of surfactants help to achieve very low IFT. Also, there is co-solvent of poly (oxy-1,2-ethanediyl), alpha-butyl-omega-hydroxy (Sulfonic L4-2) that might be used for fixing solution stability to the surfactant formulation as well as for decreasing viscosity of the interfacial emulsion. Some additional information about the abovementioned surfactants and other additives to surfactant formulation could be identified from Appendix A.

3.2 Equipment

3.2.1 Contact Angle measurement

Contact angle measurements were based on the OCA 15EC measuring unit that is made by DataPhysics Instruments GmbH, Filderstadt (Figure 13). Namely, we used the captive bubble method, where core pellets were placed into the medium of the studied fluid samples and an oil drop was injected by syringe from the bottom of this core pellet. The oil drop rose and attached to the surface of the core pellet due to the density difference between the oil drop and water medium. Thus, the contact angle was recorded after several minutes of stabilization of this oil drop.

Figure 13. OCA 15EC measuring unit

3.2.2 Aging Cell & Coreflooding

Core preparatory stages to reestablish its wettability were conducted on Aging Cell Apparatus (ACA 700) by Vinci Technologies (Appendix B). Initially, core samples were saturated with the brine and then with the crude oil. Alteration in wettability supposed to occur after the placement of the core samples into reservoir conditions for a long period. Thus, wettability could be changed from a water-wet condition to a mixed-wet condition. Likewise, coreflooding was conducted by the consequent injection of different fluids into the core sample (HSW, LSW, and LSS). The whole system could be schematically illustrated as in Figure 14. During work with this unit confining pressure was set to about 1500 psi, back pressure to nearly 500 psi and the injection flow rate was altered from 0.5 cc/min to 10 cc/min in order to overcome capillary end effect. Also, to achieve reservoir conditions and increase the temperature of the system heating mantles were used and set to 80^{o}C.

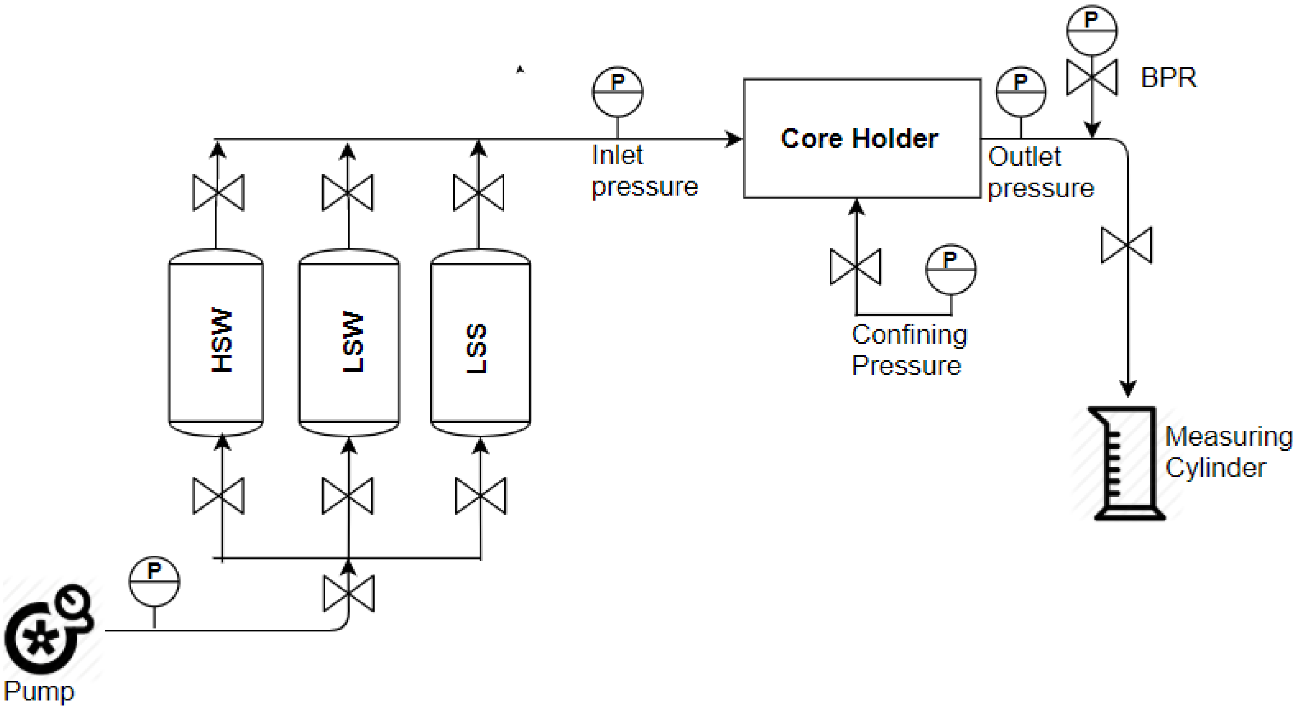


Figure 14. Coreflooding scheme

3.3 Procedure

3.3.1 Contact angle measurement

To restore initial conditions of reservoir rock, core samples were inserted into the formation water of the Tengiz field in the salinity of 180 g/L for aging for 3 days at 80^{0}C. Then to alter wettability towards oil-wet condition samples were aged by the crude oil at 80^{0}C for 30 days. Eventually, core samples were inserted into different brines for 5 days to study the most optimized dilutions or the best ionic composition for wettability alteration with the help of contact angle measurements. Here captive bubble method was used, when calcite pellets were placed into aqueous solution on the special transparent vessel for contact angle measurement and from the bottom by syringe oil droplet was added. Moreover, for higher accuracy of the contact angle recording, 3 measurements from both sides of the core pellets were made and average value evaluated. Thus, the oil/water contact angle was measured after each step and the highest contact angle difference gave the most desirable fluid sample with altered wettability towards the water-wet condition.

3.3.2 Aqueous stability & Phase behavior study

For any brine with the fixed composition, aqueous stability and phase behavior tests on surfactants were conducted. At these surfactant screening tests, the highest stability of surfactant and the best condition for the development of the microemulsion phase were studied. Hence, we analyzed different samples to obtain a clear dissolution of surfactants in the brine without precipitations and to achieve the largest microemulsion middle phase.

Samples with different ratios of XOF-314C co-surfactant to surfactant XOF-25S and XOF-26S were prepared. We selected ratios in the range of 30/70, 40/60, 45/55, 50/50, 70/30, and 100/0. Aqueous solutions were prepared in the different ratios of co-surfactant/surfactant that added to distilled water and mixed with the magnetic stirred for an hour at 800 rpm. For each case, samples were poured into 10 mL glass burettes and placed in reservoir conditions as well as in ambient conditions. After 3 days and 7 days, samples were traced. The most optimal aqueous stable surfactant formulation was identified visually by the clarity of black lines in the background as in Figure 15.

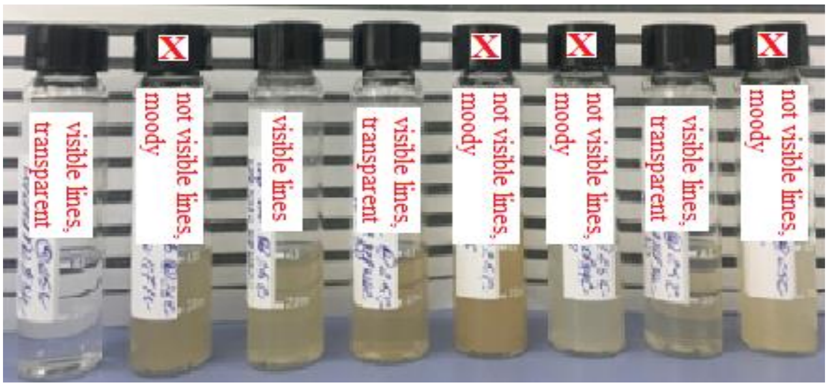


Figure 15. Aqueous Stability Test criteria

The same procedure was applied for surfactants provided by Sasol with no co-solvents and with only pure surfactants at 1 wt% concentration. All solutions were prepared with 1wt% to see aqueous stability at ambient room temperature of 25^0C and a reservoir temperature of 80^0C.

Samples with acceptable stability were screened at this stage for the further phase behavior tests, where an equal amount of crude oil (2ml) and surfactant solution (2ml) were added into the 10ml burette. The mixtures were shaken mechanically about 10 min and after 3- and 7-days samples were traced at both temperature ranges. Namely, oil/brine solubility and appearance of Winsor type III microemulsion were analyzed. Finally, the samples giving the highest microemulsion ratio were screened and chosen for further studies.

3.3.3 Coreflooding

After characterization stages, some surfactant samples have been eliminated and the best ones were selected due to the best performance in contact angle measurement, aqueous stability, and phase behavior tests. It means that more optimized ones according to the most change in the contact angle value and existence of the middle phase were identified. Then to observe incremental oil recovery provided by the combined method coreflooding was required. There were a few preparatory steps of the core. Namely, cutting with a length of 3 inches were cleaned with distilled water and dried in the oven for 24 hours. Its porosity measured with gas (Nitrogen) and with liquid saturator. Similarly, to mimic initial conditions of the core sample it was flooded with the high saline brine, where absolute permeability to water was identified and then with crude oil, where relative permeability to oil was recorded. Afterward, it was inserted into crude oil in the oven at 80^0C to reestablish its wettability for 5 weeks. To increase the oil saturation of the core sample and produce extra water one more oil flooding was conducted. Then the core was flooded with sequences of HSW (high saline formation brine), LSW (low saline smart water) and hybrid low saline surfactant brine, where the enhanced impact of the proposed method could be identified from analysis of the recovery factor.

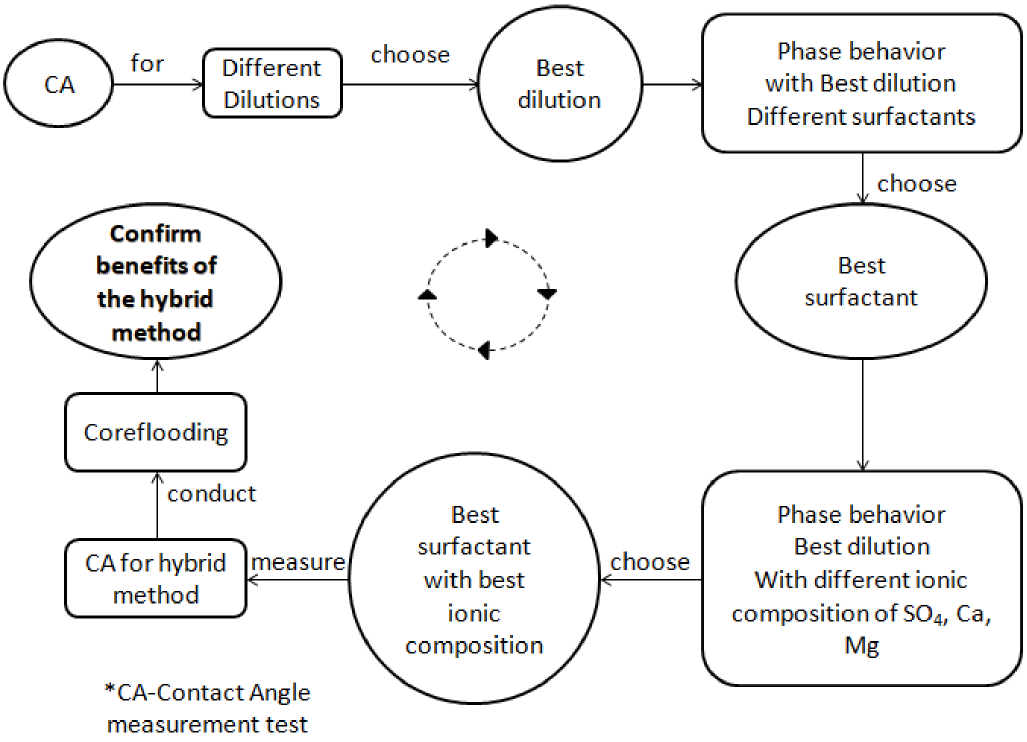


Figure 16. A general roadmap of experiments

Thus, the screening and design are based on the results obtained from the numerous experiments of contact angle measurement, aqueous and thermal stability, phase behavior, and coreflooding. The general procedure is illustrated in Figure 16. Namely, there was a sequence of these experiments for the determination of the best dilution of SW. It was followed by aqueous stability and phase behavior tests at a certain dilution of various surfactants to identify the best surfactant formulation. Then for determination of the most optimized ionic composition, different fluid samples were prepared and their effects on contact angle alteration, aqueous stability and phase behavior were tested. Thus, the oil displacement by the proposed hybrid method with optimized ionic composition and chosen surfactant was studied by the coreflooding experiment. Consequently, from observations on the oil recovery, the efficiency of the hybrid method could be confirmed as it is depicted in a general roadmap shown in Figure 16.

CHAPTER-4: RESULTS AND DISCUSSION

4.1 Contact angle measurement and determination of the best dilution of SW

Wettability alteration towards the water wet condition of the core samples has been traced. Its indicator is in terms of a contact angle difference, where a change in wettability was measured after crude oil aging and after aging with different dilutions of the original brine. These recordings are listed in Table 11. They were made by the captive bubble method as shown in Figure 17, where an enlarged snapshot of oil drop attached to the carbonate pellets is illustrated.

Table 11. Contact angle measurement at different dilutions

Dilution	**Initial contact angle**	**Final contact angle**	**Contact angle difference**
Base	94	103	9
2X	94	112	18
10X	94	115	21
20X	94	111	17

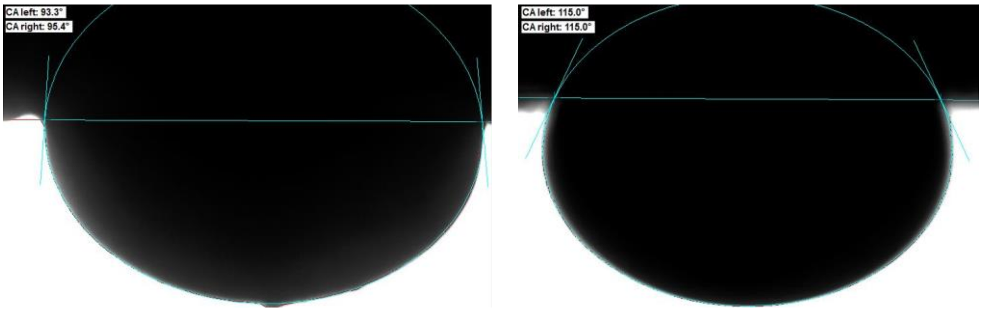


Figure 17. Contact angle measurement by OCA 15EC at 10X dilution in the left side initial one after crude oil; in the right side after 10X dilution aqueous solution

Thus, the highest alteration in the contact angle could be admitted from Figure 18. The optimum one with the highest contact angle difference has been identified to be 10X diluted Caspian Sea that is used for further stages of the study.

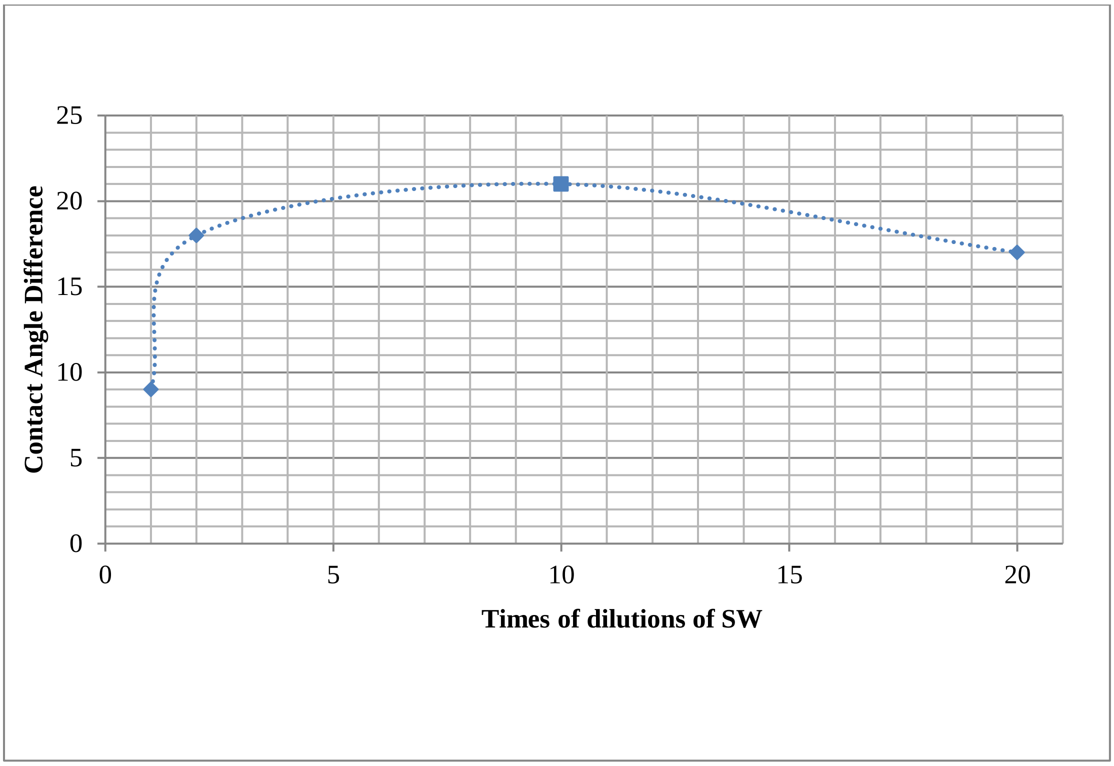


Figure 18. Contact angle measurement for the best dilution determination

4.2 Aqueous stability & Phase behavior

Numerous experimental observations of aqueous and thermal stability have been implemented in this study. Co-solvent of Sulfonic L4-2 also added as it has been advised by suppliers in a range from 0.2 wt% to 0.5 wt%. However, there was no significant change in the transparency of the samples, in the visibility of black lines at the background, and it has been decided for simplicity of the surfactant formulation to proceed without co-solvent variation. Thus, there were various surfactant formulations with the only surfactant to co-surfactant ratios as it is depicted in Table 12. At this stage surfactant combinations were screened at 10X diluted SW.

Table 12. Surfactants screened at 10X diluted SW

Surfactant	**Surfactant ratio**	**Co-surfactant XOF314C ratio**	**Salinity, ppm**
XOF-25S	30	70	1300
	40	60	1300
	45	55	1300
	50	50	1300
	70	30	1300
	1	0	1300
XOF-26S	30	70	1300
	40	60	1300
	45	55	1300
	50	50	1300
	70	30	1300
	1	0	1300
Soloterra 113H	1	0	1300
Soloterra 117H	1	0	1300

Initially, XOF-25S and XOF-26S samples and XOF-314C samples with a surfactant to co-surfactant ratios varied from 30/70 to 50/50 were analyzed. The corresponding test of aqueous stability could be seen in Figure 19. Samples were traced after 3 days at the reservoir and ambient temperatures. The ones without precipitations and more transparent at both temperature ranges were considered as stable. Thus, samples marked with red arrows in Figure 19 passed the stability criteria.

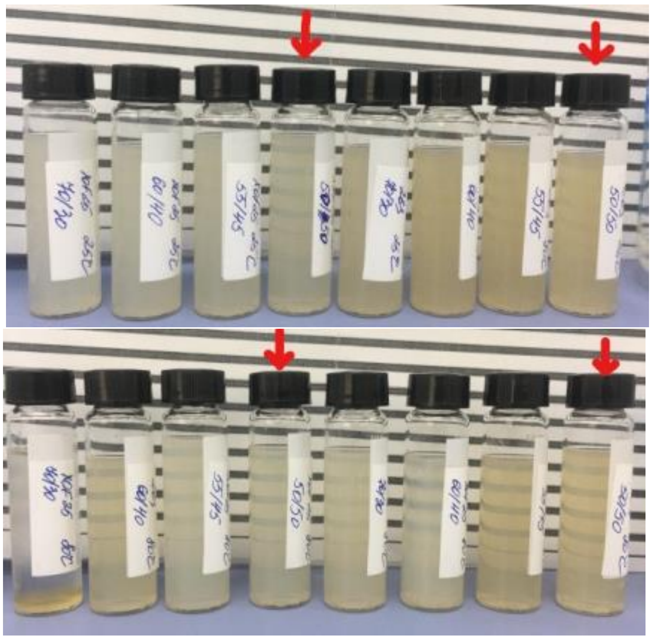


Figure 19. a. Aqueous stability after 3 days at 25^{0}C (upper one); b. aqueous stability after 3 days at 80^{0}C (lower one) surfactant to co-surfactant ratio varied from 30/70 to 50/50

Moreover, tests continued with an increased amount of surfactant to the co-surfactant ratio from 50/50, to 70/30 and to 100/0. The procedure for the behavior of the samples recorded as in the previous set and is shown in Figure 20.

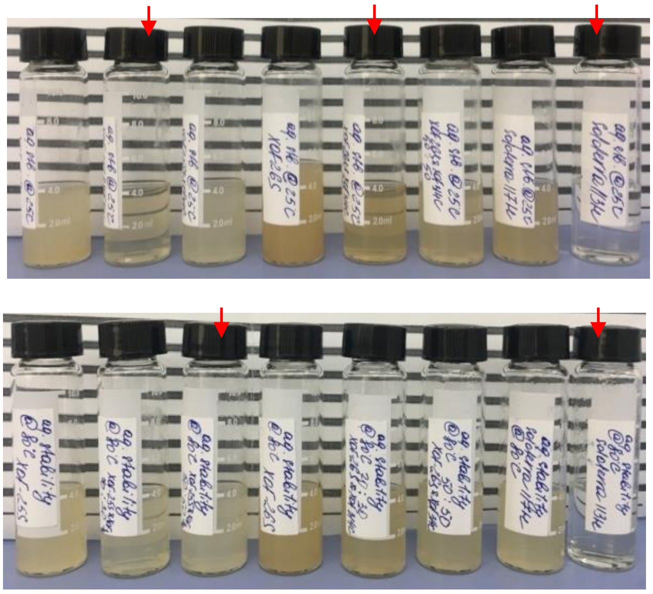


Figure 20. a. Aqueous stability after 3 days at 25^{0}C (upper one); b. aqueous stability after 3 days at 80^{0}C (bottom one) of various surfactants

As a result of qualitative visual tests on the abovementioned samples, more transparent solutions with visible black lines at background have been identified. From them, it could be deduced that the most aqueous stable surfactant formulations were XOF-25S & XOF-314C in the ratio of 70/30 and 50/50. Also, it was similar to XOF-26S & XOF-314C. While for Sasol products the one identified as the aqueous stable was Soloterra 113H.

The next stage of the surfactant screening procedure was an analysis of the phase behavior that is illustrated in the Figures below. From these tests' solubility of the oil and water phases was identified at ambient and reservoir temperatures after 3 days.

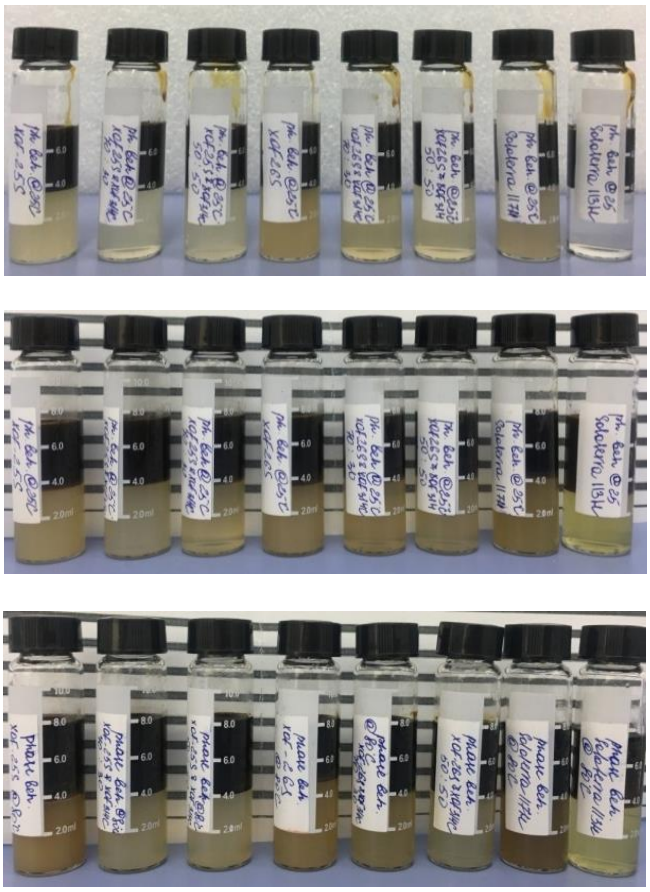


Figure 21. a. Initial phase behavior (in the upper side); b. phase behavior after 3 days at 25^0C (in the middle); c. phase behavior after 3 days at 80^0C (in the bottom one)

To quantify the performance of the surfactant solubility, the height of the middle phase was recorded and the microemulsion ratio was plotted in Figure 22. Here behavior of various surfactant formulations at 10X dilution of SW checked.

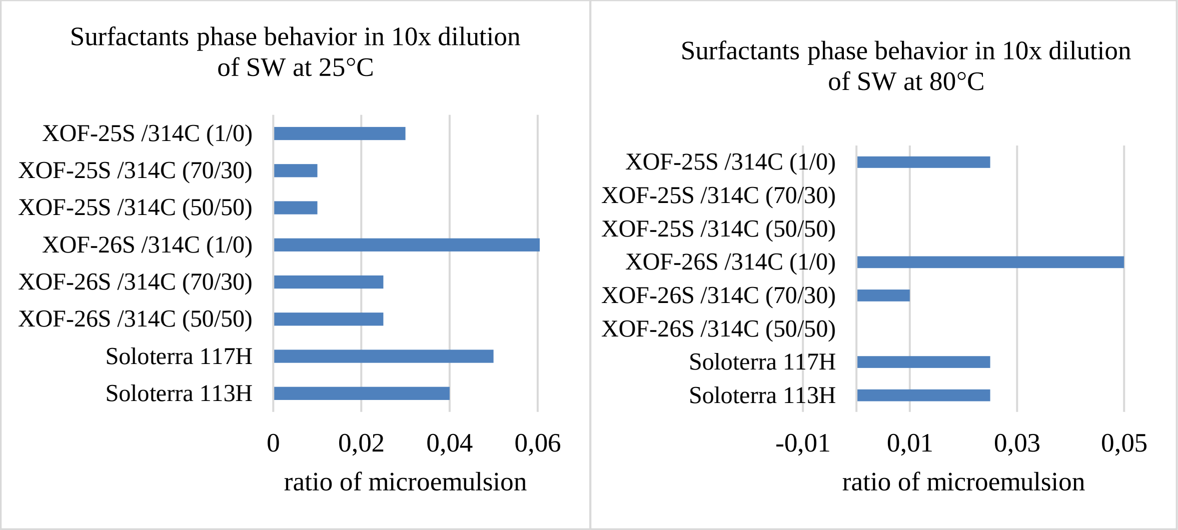


Figure 22. a. Surfactants phase behavior in 10x dilution of SW at 25°C after 3 days (on the left side); b. Surfactants phase behavior in 10x times dilution of SW at 80°C after 3 days (in the right side)

Thus, tests of aqueous stability and phase behavior are summarized in Table 13. Samples with plus are passing a certain test of aqueous stability or phase behavior with desirable performance. In other words, for aqueous stability to be plus, it means that they are stable at reservoir temperature without precipitation and visible black lines at the background of burettes are confirming stability. While, for samples to pass phase behavior test at reservoir temperature after 3 days, it's enough to have any ratio of microemulsion (Winsor type III) at this stage.

Table 13. Aqueous stability and phase behavior of surfactants at 10x dilution of SW

Total surfactant concentration 1wt% /ratios	**XOF-25S & XOF-314C**			**XOF-26S & XOF-314C**			**Soloterra/117H**	**Soloterra/113H**
	1:0	70:30	50:50	1:0	**70:30**	50:50		
Phase behavior and presence of middle phase at res.cond. (yes+, no-)	+	-	-	+	+	-	+	+
Aqueous stability at res.cond. (yes+, no-)	-	+	+	-	+	+	-	+

Therefore, it has been suggested to proceed with Soloterra 113H and XOF-26S/XOF-314C (in the ratio of 70 to 30) surfactants for further experiments that passed both requirements of phase behavior and aqueous stability tests.

4.3 Phase behavior and Contact angle measurements to determine the effect of active ions

The selected surfactants behavior of XOF-26S/314C and Soloterra 113H could be checked in the altered ionic composition. Salinities of these aqueous solutions with different ionic compositions are depicted in Table 14.

Table 14. Different brine samples with different ionic composition and salinities

Brine samples / **Surfactants**	**10xSW-S, Mg, Ca**	**10xSW-0S, Mg, Ca**	**10xSW-4S, 2Mg, 2Ca**	**10xSW-4S, 2Mg, Ca**	**10xSW-4S, Mg, 2Ca**	**10xSW-6S, 3Mg, Ca**	**10xSW-6S, Mg, 3Ca**	**10xSW-8S, 4Mg, 4Ca**
XOF26S/314C (70/30)	0.13	0.1	0.16	0.23	0.22	0.3	0.29	0.37
Soloterra 113H	0.13	0.1	0.16	0.23	0.22	0.3	0.29	0.37

From literature, it has been identified that Mg, Ca and SO_4 role in wettability alteration is crucial. However, there are numerous combinations of these ions and their impact in terms of groups has not been investigated as their individual effect. Therefore, in this thesis influence of groups of ions was checked. These groups are Mg+SO_4, Ca+ SO_4, and Mg+Ca+SO_4. Their effect on contact angle differences on carbonate rock surfaces is indicated in Table 15, where listed values corresponding to the average value of measurements of contact angle. The initial contact angle here was in the range of 90-95 degrees in the neutral wettability condition.

Table 15. Effect of different ionic groups on Contact Angle (CA) differences

Effect of Mg+SO_4			
Testing sample fluid	SWS,Mg,Ca	SW4S, 2Mg, Ca	SW6S, 3Mg, Ca
CA difference	15.6	18.9	11.8
Effect of Ca+SO_4			
Testing sample fluid	SWS,Mg,Ca	SW4S, Mg, 2Ca	SW6S, Mg, 3Ca
CA difference	15.6	19.9	21.3

Effect of $Mg+Ca+SO_4$			
Testing sample fluid	SWS,Mg,Ca	SW4S, 2Mg, 2Ca	SW8S, 4Mg, 4Ca
CA difference	15.6	18.4	10.2

Consequently, based on the recordings of contact angle differences at various ionic groups, their impact on wettability alteration has been deduced. The amounts of positive ions as magnesium and calcium were essential in the detachment of carboxylic groups of oil particles. For instance, small concentration was not enough to change wettability by reacting with oil particles, while too high concentration might repulse with positively charged carbonate surface and be useless or even could react with other elements and precipitate.

Another essential wettability influencer was negatively charged sulfate ion. It reduced positive charge of the carbonate surface and it helped in detachment of oil particles by positive ions of magnesium and calcium. Thus, there were a certain number of above-mentioned ions that changed the wettability of oil-wet the core samples towards the water-wet condition. The highest alteration was corresponding to optimal ions concentration. In the $Mg+SO_4$ group optimal ionic composition was at 10xSW_4S, 2Mg, Ca that gave the highest contact angle alteration of 18.9 degrees (Figure 23A). Another ionic group of $Ca+SO_4$ changed the wettability of the core pellets towards the water-wet condition with increased ions concentration. Thus, the most optimal ions composition among measured ones was identified at 10xSW_6S, Mg, 3Ca that was corresponding to 21.3 degrees (Figure 23B). These two groups of $Mg+SO_4$ and $Ca+SO_4$ were differentiated only by the respective amount of divalent ions, while sulfate ions kept the same. Therefore, it could be noted that spikes in the concentration of calcium ions were more effective in changing the wettability of the studied carbonate core samples compared to magnesium ions. Too many active ions of magnesium had an adverse effect on the change of wettability. Similarly, the combined effect of the $Mg+Ca+SO_4$ ionic group had a significant decrease in the contact angle difference at the high amount of active ions. Its optimal number of active ions was corresponding to the following composition 10xSW_4S, 2Mg, Ca. The overall trend is illustrated in Figure 23.

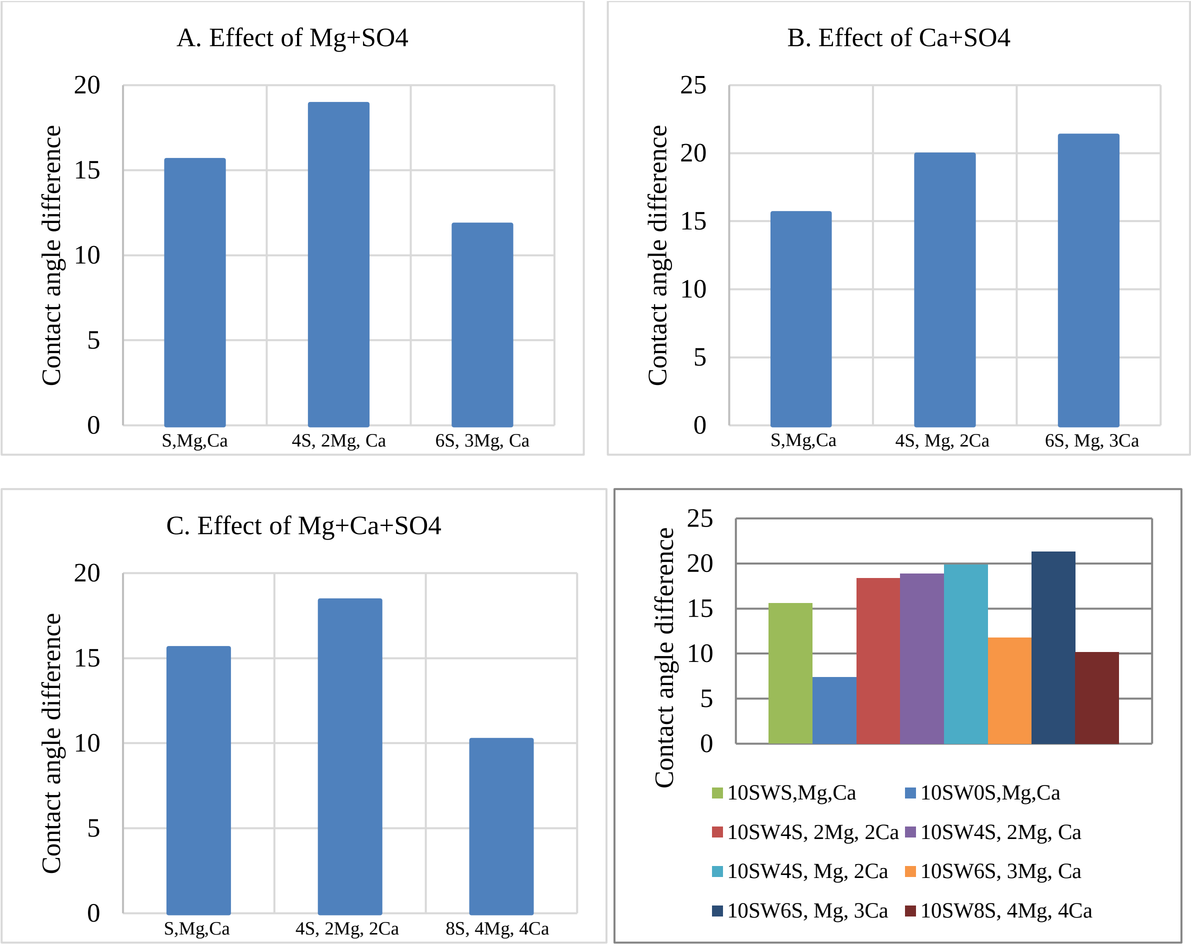


Figure 23. Effect of various ionic groups at 10SW A. Mg+SO4, B. Ca+SO4, C. Mg+Ca+SO4 on wettability alteration in terms of contact angle difference; D. All cases

Thus, the best performance of each surfactant at certain ionic compositions could be identified from the phase behavior test below. Here the microemulsion ratio was a representative indicator of the best aqueous solution composition.

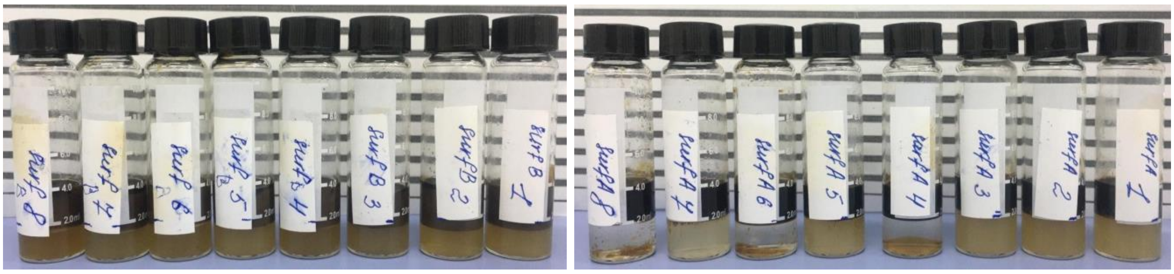


Figure 24. a. phase behavior for surf B (Soloterra 113H) after 3 days at 80^0C in the left side b. phase behavior for surf A (XOF-26S/314C in 70/30 ratio) after 3 days at 80^0C in the right side

Thus, the significant presence of the middle phase in both cases of surfactants recorded in the following solutions: 10xSW_6S, Mg, 3Ca (0.4 microemulsion ratio) and 10xSW_4S, Mg, 2Ca (0.05 microemulsion ratio) that could be confirmed by Figures 24 and 25. Additionally, these aqueous solutions corresponding to the highest contact angle differences of 21.3 and 19.9 degrees, respectively. It means that the chosen best smart water composition should be optimal from all experiments on contact angle measurements, phase behavior, and aqueous stability tests. Thus, the optimized performance of Soloterra 113H surfactant was recorded at the aqueous solution of 10xSW_6S, Mg, 3Ca, while for XOF-26S/314C surfactant optimized behavior was corresponded to 10xSW_4S, Mg, 2Ca.

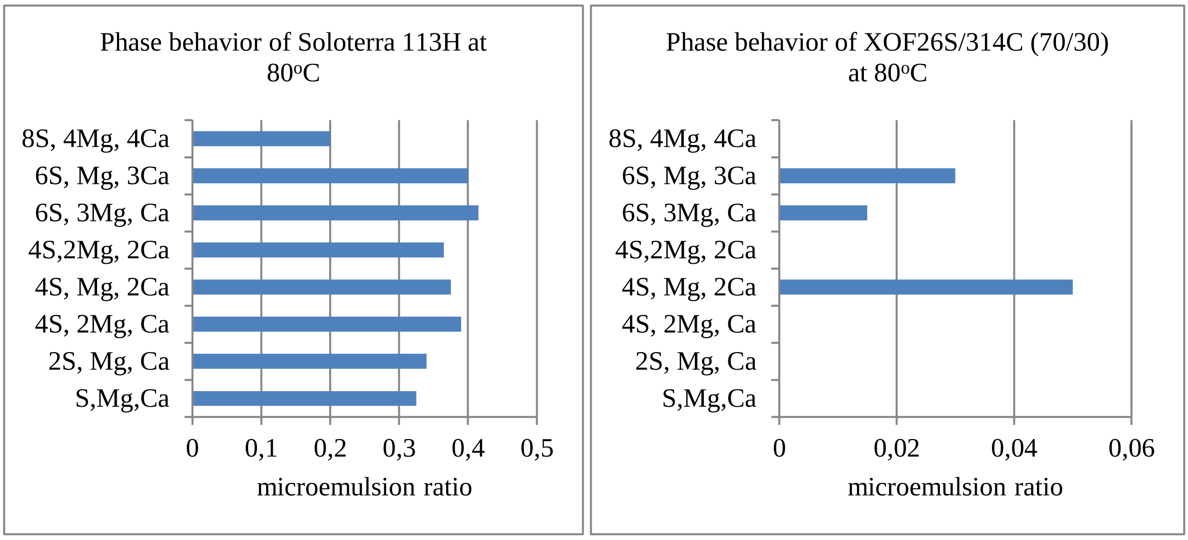


Figure 25. a. Microemulsion ratio of Soloterra 113H at 10SW with changed ionic composition; b. Microemulsion ratio of XOF-26S/314C (70/30) at 10SW with changed ionic composition

The best water compositions have been chosen for both surfactants. Now we could use them in combination with surfactants to analyze the wettability alteration effect. From Figure 26 of contact angle measurements, it could be admitted that their combination is more effective in terms of wettability alteration towards the water-wet condition. For instance, the contact angle differences of the considered hybrid method could be compared to the separate usage of surfactant at SW only or to the smart water effect on wettability alteration without surfactant. For both surfactants, it gave nearly 10^0 advancement in contact angle difference compared to standalone LSW and almost 15 degrees difference compared to surfactant at SW only.

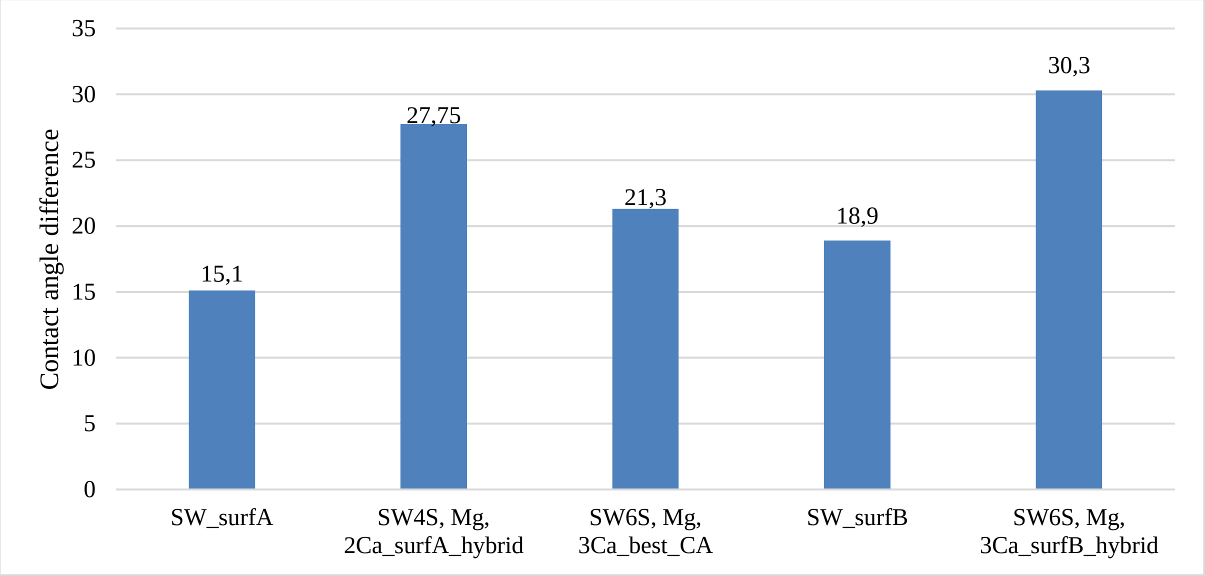


Figure 26. Final Contact Angle Measurement of the hybrid methods

The choice of the surfactants narrowed from the beginning to two main formulations. It could be pointed out that the hybrid method was relatively better than the separate effect of low saline waterflooding or surfactant flooding as it is depicted in Table 16.

Table 16. Choice of the hybrid method

Solution / **Test**	**Soloterra 113H with 10SW_6S,Mg,3Ca**	**XOF-26S/314C with 10SW_4S,Mg,2Ca**	**Soloterra 113H in SW**	**XOF-26S/314C in SW**	**10SW_6S,Mg,3Ca or 10SW_4S,Mg,2Ca**
Aqueous stability	+ (more transparent)	+ (moody)	+	+	+
Microemulsion ratio	+ (0.4)	+ (0.05)	-	-	-
CA difference	30.3	27.75	18.9	15.1	21.3 or 19.9

However, it should be admitted that the performance of Soloterra 113H surfactant was significantly better than of the XOF-26S/314C because of higher microemulsion ratio (higher solubility) and better aqueous stability as it has been summarized in Table 16.

Moreover, IFT could be calculated from the solubilization ratio by Chun-Huh equation (c=0.3mN/m) as it is shown in Figure 27. IFT between oil and surfactant phase is corresponding to Ϭ_mo, while IFT between water and surfactant is corresponding to Ϭ_mw. It was pointed out that there was no Winsor type III microemulsion in the Caspian Sea of surfactants. Similarly, effect of the ionic alterations of the chosen smart water compared to the base case of 10 times dilution of SW in terms IFT reduction. The combination of soloterra 113H with 10SW_6S,Mg,3Ca corresponds to the lowest IFT as it is indicated in the left side in Figure 27.

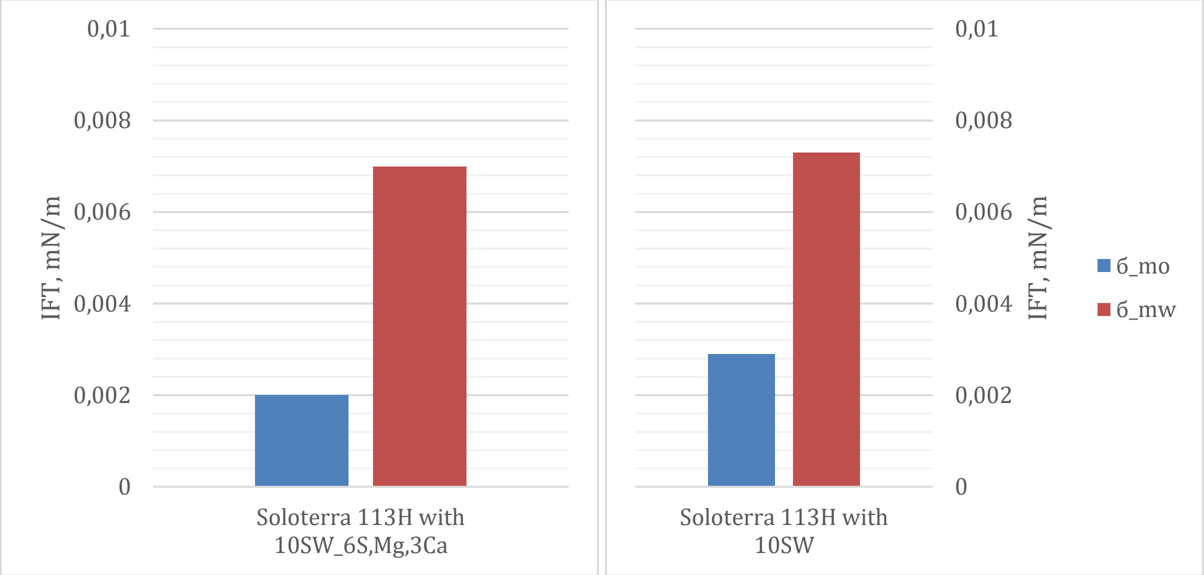


Figure 27. IFT for the hybrid methods

Thus, in the next stage of coreflooding only the best surfactant that was Soloterra 113H in combination with the brine composition of 10SW_6S,Mg,3Ca was used. The proposed hybrid method here is surfactant Soloterra 113H at 10xSW_6S, Mg, 3Ca aqueous solution that was beneficial from aqueous stability, phase behavior and wettability alteration points of view.

4.4. Coreflooding

At this stage benefits of the proposed hybrid LSW/LSS method could be analyzed in terms of incremental oil recovery. Some preliminary tests as a measurement of the physical properties of the core as porosity via gas (Nitrogen) and with saturator were implemented and obtained data is in Table 17.

Table 17. Limestone core properties

Core	**m_{dry}, g**	**L, mm**	**D, mm**	**$Ø_{He}$, %**	**V_p,**	**M_{wet}, g**	**$Ø_{sat}$, %**	**k_{abs},**
1	177.23	71.45	38.27	19.41	15.95	194.81	15.61	16

P_{brine}=1.126 g/cc

The next preparatory stage was the identification of absolute permeability to water when high saline brine was injected. Here recordings of the pressure difference were correlated with a pore volume of injected fluid by Darcy law. As a result, the slope in Figure 27 corresponds to the absolute permeability of brine that is 16.015 mD.

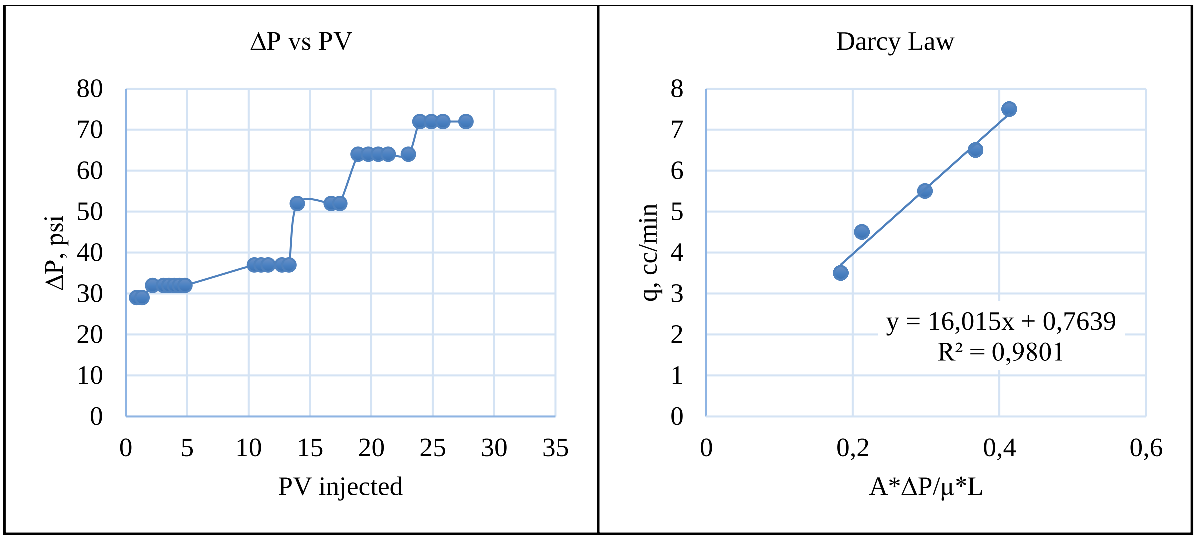


Figure 28. Absolute permeability to water

Then, crude oil was injected. Similarly, to the previous injection pressure difference versus injected pore volume of crude oil were recorded (Figure 28) and after stabilization of pressure, the flow rate was increased from 1cc/min till 3cc/min with a step of 0.5cc/min. However, there was no stabilization at high flow rates due to turbulences, and pressure differences continued to increase that was not included in this study. At the end of the test when pressure stabilized and only oil production occurred Darcy law was used for evaluation of effective permeability to oil that was 10.589 mD.

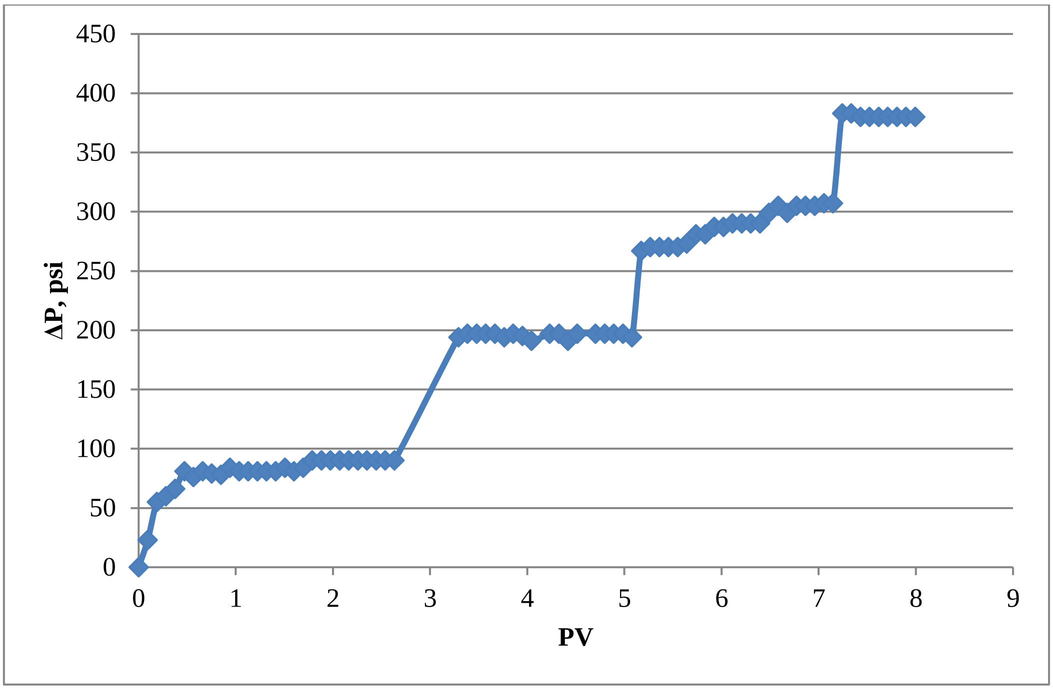


Figure 29. Pressure difference during pore volumes of crude oil injected

Also, during the injection of crude oil produced brine amount was recorded for the determination of Swi. It can be seen from Figure 29. The trend of water production versus the injection of crude oil indicated the amount of produced water that was equal to 10.7 ml. By measuring the dead volume of the tubing that was 0.8 ml, the actual produced volume of brine reduced to 9.9 ml. Thus, Swi became 37%. The core sample was then placed into the oven for 5 weeks at 80^{o}C and flooded with crude oil again to produce extra water as well as to obtain higher initial oil saturation (Soi) before coreflooding. However, no more water produced and Swi remained 37%.

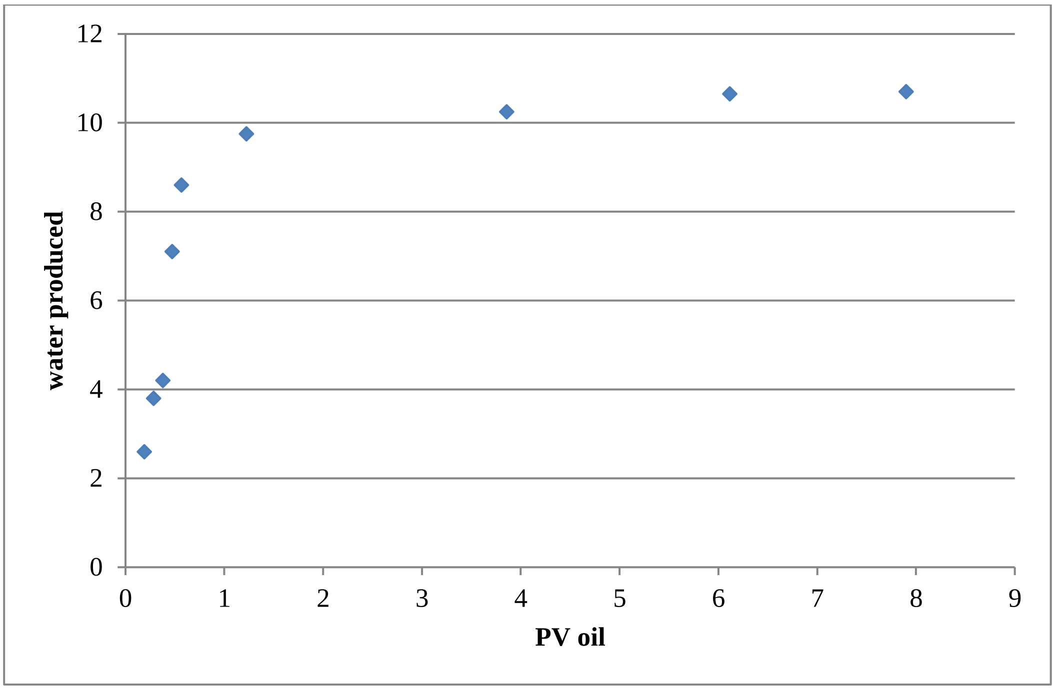


Figure 30. Water produced vs PV oil injected

Then implemented coreflooding test justified benefits of the suggested hybrid method. Namely, enhancement in production of the proposed hybrid method has been observed from the consequent injection of HSW, LSW (low saline smart water of 10xSW_6S, Mg, 3Ca) and hybrid low saline surfactant (10xSW_6S, Mg, 3Ca with Soloterra 113H) flooding. The alteration from one fluid to another occurred when no more oil production happened after the injection of several pore volumes. Also, another valid indicator was the stabilized pressure difference. It has been decided to set the injection rate to 0.5 cc/min to have recordable pressure difference, and then to overcome capillary end effect flow rate was increased to 5 cc/min. Recordings of pressure differences are illustrated in Figure 30. Initially, pressure difference after HSW at 5cc/min was 58 psi and at the end after hybrid method injection at 5cc/min reduced to 9 psi that could be explained by viscosity difference of oil and brines.

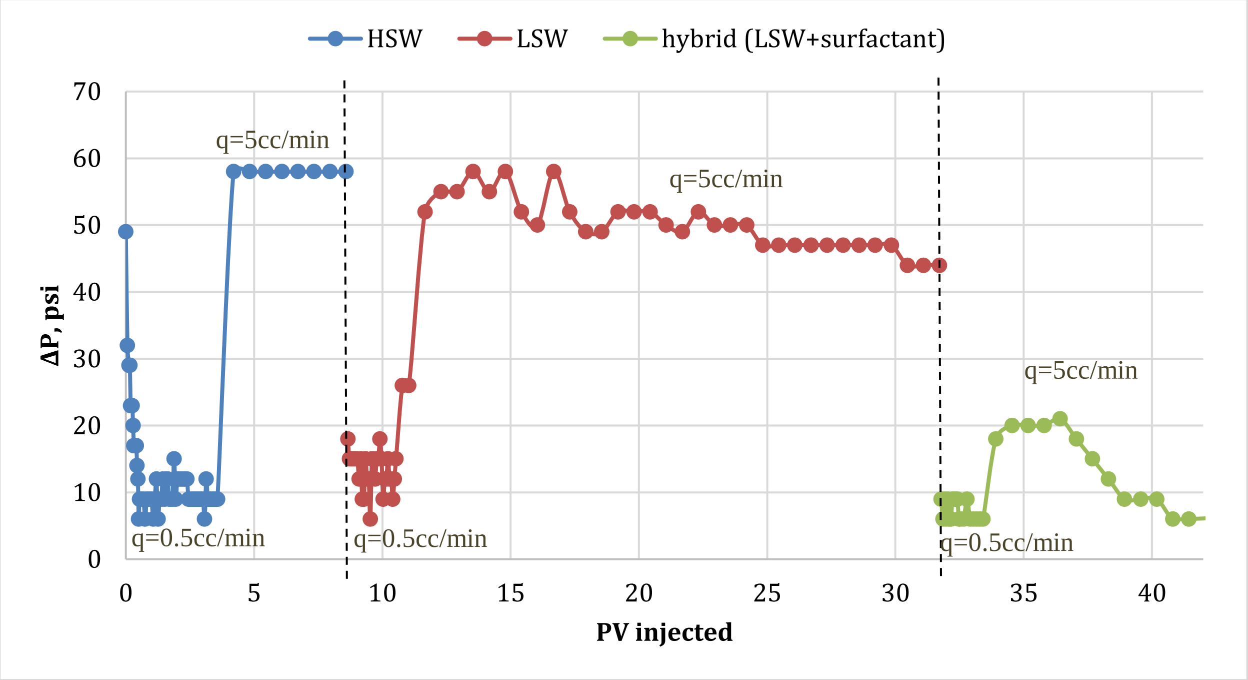


Figure 31. Pressure difference at various PV injected

Now from Figure 31 oil recovery trend could be traced. Initially, oil recovery after HSW was about 52%. Then oil recovery increased by 9% after injection of nearly 20PV of the engineered brine with the ionic composition of 10xSW_6S, Mg, 3Ca in the secondary recovery mode. Moreover, it could be pointed out that nearly 6PV of the hybrid fluid (LSW+surfactant) required for enhancement of the oil recovery and achieving a production plateau. Here incremental oil recovery provided by the hybrid LSW/LSS EOR method was almost 10%. Thus, in total 70% of oil originally in place was recovered after tertiary injection of the hybrid method.

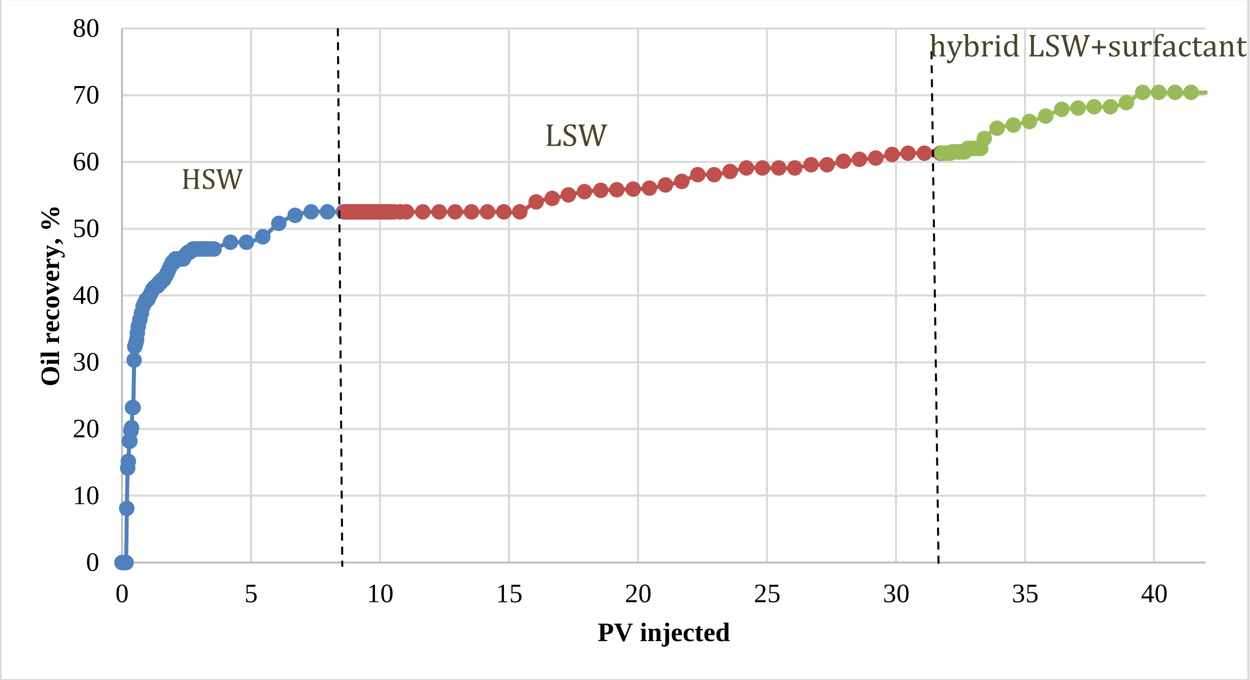


Figure 32. Oil recovery at various PV injected

Thus, obtained results justified flooding scenario of HSW, LSW, and LSS with noticeable enhancements in production after secondary and tertiary injections.

CHAPTER-5: Conclusions and Recommendations

The main objective of the study was to screen and design the hybrid LSW/LSS method. To fulfill the designated goals of the study numerous experiments have been conducted. These tests mimic Kazakhstani oil fields with carbonate core samples, with local crude oil and brine samples. Wettability alteration, aqueous stability, the solubility of the oil/water interfaces and oil recovery efficiencies were analyzed via contact angle measurement, phase behavior, and coreflooding tests, respectively. Thus, this study summarizes the next findings:

- The optimized dilution of SW with the highest change in contact angle towards water-wet condition was at 10 times diluted SW (10xSW), while the optimized ionic composition of ‘Smart Water’ corresponded to 10XSW with 6- and 3-times sulfate and calcium ions (10xSW-6SO_4, Mg, 3Ca) that changed the contact angle to more than 20°.
- Soloterra 113H (Alkyl Benzenesulfonic acid) was defined as the most suitable surfactant that showed the best solubilization ratio, aqueous stability, and Winsor type III after 3 and 7 days of observation.
- The proposed hybrid engineered brine/surfactant combination was a 10xSW-6SO_4, Mg, 3Ca with Soloterra 113H that was chosen according to optimized wettability alteration, aqueous stability, and high solubility of oil/water interfaces. It shifted the contact angle 10° more to the water-wet state in comparison to the standalone optimized brine. The microemulsion phase volume was also increased by 40% compared to the only surfactant.
- From the coreflooding test it was identified that in total 70% of oil originally in place (microscopic sweep efficiency) recovered after tertiary injection of the hybrid method, while incremental oil recovery provided by the hybrid LSW/LSS was almost 10%.
- Promising results obtained in this study make the proposed hybrid LSW/LSS method relevant and attractive for further investigations.

In future work, more coreflooding tests could be implemented to study various injection scenarios. Also, by this coreflooding test other engineered brine/surfactant combinations could be analyzed. Further enhancement in the performance of the hybrid method could be achieved by polymer incorporation into the hybrid EOR method that would improve mobility control. Thus, more tests should be conducted with a low saline surfactant-polymer hybrid method.

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APPENDIX

Appendix A

Name	**Type of Chemical**	**Chemical formulation**	**Physical state**	**pH**	**Boiling/Cond. Point @25^{0}C**	**Flash point**	**Chemical stability at normal cond.**
XOF-25S	Surfactant /Huntsman Activity: 25 %w/w	Benzenesulfonic acid, dimethyl-, mono-C11-16- alkyl deriv., sodium salts	Liquid	7	100 ^{o}C	>100 ^{o}C	Stable
XOF-26S	Surfactant /Huntsman Activity: 25 %w/w	Benzenesulfonic acid, C14-24-branched and linear, alkyl deriv., sodium salts	Liquid	7	100 ^{o}C	>100 ^{o}C	Stable
XOF-314C	Co-surfactant /Huntsman Activity: 25 %w/w	Oxirane, methyl-, polymer with oxirane, mono(2,4-dinonylphenyl)ether Sodium chloride	Liquid, color white, odour like soup	10.66	Water solubility <500 mg/L, density 1.0126 g/cm3, kinetic viscosity 2034 mm2/s	Method closed cup	Stable
Sulfonic L4-2	co-solvent /Huntsman Activity: 100 %w/w	Poly(oxy-1,2-ethanediyl), alpha-butyl-omega-hydroxy	Liquid	7.2	120 ^{o}C; density– 0,9622, viscosity kinematic– 7.54cSt;	Method closed cup 64.2 ^{o}C	Stable
Soloterra/ 117H	Surfactant/Sasol Activity: 92.3%w/w	Benzenesulfonic acid, 4-C15-16-sec- alkyl deriv.,	Dark viscous liquid	<2	density– 1.002g/cm3, viscosity kinematic– 779.2 mm2/s	206.9 ^{o}C	Stable
Soloterra/ 113H	Surfactant/Sasol Activity: 96.5%w/w	Benzenesulfonic acid, 4-C10-13-sec- alkyl deriv.,	Brownviscous liquid	<2	density– 1.06g/cm3, viscosity dynamic– 2400 mPas	210 ^{o}C	Stable