

Solvent retrieval and wettability alteration during heavy-oil and bitumen recovery by
SOS-FR (steam-over-solvent injection in fractured reservoirs) method

by

Mohmmedalmojtaba Yousri Salama Mohammed

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Department of Civil and Environmental Engineering
University of Alberta

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Abstract

Water injection is inefficient to recover heavy oil from naturally fractured carbonate reservoirs mainly due to its oil-wet nature of the matrix. Solvent injection could be an option in this type of reservoir through dilution of oil and gravity drainage. This, however, will only be feasible if the injected solvent is retrieved back effectively. This thesis focuses on the two approaches that can be used to retrieve the solvent diffused into matrix: (1) Thermal method and (2) chemical methods.

In the thermal method, steam or hot water is injected at or around the bubble temperature of the solvent. The solvent will then be retrieved by its vaporization, which was the base of a recent suggested method called steam over solvent injection in fractured reservoirs (SOS-FR) method (Al-Bahlani and Babadagli, 2008). An experimental setup that enables quantifying the retrieved solvent at the end this process was designed and then used to investigate the effect of different factors on the process. Then, an optimization study was performed to determine the optimal conditions for oil recovery and solvent retrieval during the SOS-FR method.

Chemical methods rely on the possibility of altering the wettability of rock surfaces. This type of treatment is a new approach to develop heavy oil/bitumen containing oil-wet systems. After a critical review of the past literature in wettability alteration with a comprehensive analysis of materials/methods suggested for different types of reservoirs, selected chemicals were tested on heavy-oil saturated core samples pre-exposed to solvent. The chemicals tested include surfactants, high pH solutions, low/high salinity water, nanofluids, and ionic liquids. The key parameters to evaluate the efficiency of the examined recovery methods were oil recovery and solvent retrieval through enhanced capillary imbibition.

This thesis is dedicated to my youngest brother Ibraheem. Just to let him know "dreams cannot come true, you force them!"

(رب زوني علماً) [طه:114]

“O' Lord! Increase my knowledge”(Qur'an;20:114)

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CHAPTER 1: INTRODUCTION

Introduction

Thermal enhanced oil recovery methods (most notably steam injection) have been widely used to recover heavy-oil from sandstone reservoirs. Different versions of hybrid thermal-solvent recovery methods have also been proposed in literature to increase the efficiency of heavy-oil recovery by reducing the amount of steam used. For example, solvent injected with steam can help to minimize the required energy during steam assisted gravity drainage (SAGD) process (Li et al., 2011a-b; Nasr et al., 2003), while the combination of solvent and steam injection was suggested to benefit from the wormholes created after Cold Heavy Oil Process with Sand (CHOPS) (Rangriz-Shokri and Babadagli, 2012a-b). When solvent is used solely or in combination with a thermal method, the main challenge is to retrieve the injected solvent due to its high cost. This means the feasibility of any hybrid or sole solvent injection method relies on two factors: oil recovery and solvent retrieval. However, these processes usually are not easily applicable for naturally fractured carbonate reservoirs, where most of the oil is stored in oil-wet matrix and the fracture network only controls the flow. Recently, Al-Bahlani and Babadagli (2008) developed a new approach named SOS-FR (steam-over-solvent injection in fractured reservoirs) to recover matrix oil in naturally fractured reservoirs. They observed very positive responses at the field scale (Al-Bahlani and Babadagli, 2010) with high ultimate recoveries. The efficiency of this process, however, is purely determined by the amount of solvent retrieved at the end of the process, which is done mainly by injecting steam/hot-water at the bubble point of the injected solvent. Hence, the injected solvent is retrieved during SOS-FR by thermal means mainly because of the oil-wetness of the Naturally Fractured Carbonate Reservoirs (NFCRs).

If one is able to change physiochemical properties of the matrix of the NFCRs, on the other hand, solvent can be retrieved without the need to apply a thermal phase. Additional oil may also be recovered during the imbibition/drainage process. Chemically induced wettability alteration was extensively researched in literature for light oil reservoirs but such efforts are lacked for heavy oils. To select the potential wettability alteration methods for NFCR containing heavy-oil, a comprehensive analysis of chemicals is needed, highlighting their limitations and the applicability.

Statement of the Problem

With continuous depletion of conventional oil reservoirs around the world, increasing attention has been drawn to unconventional oil resources around the world with an eye towards 536 billion barrels of bitumen located in carbonate formations in Alberta, Canada. An efficient technology to unlock these promising resources is yet to be discovered. The application of primary and secondary recovery processes in these Naturally Fractured Carbonate Reservoirs containing heavy-oil/bitumen usually results low recovery factor and an Enhanced Oil Recovery method

(EOR) is mostly needed at early stages. Solvent injection is considered one, if not the most, efficient EOR in this type of reservoir. Hatiboglu and Babadagli (2008) tested the efficiency of solvent injection in different types of rock samples. More recently, Al-Bahlani and Babadagli (2010) published experimental results that showed that the feasibility of solvent injection can be improved by providing the ability of solvent retrieval at the end of the process by injecting steam or hot water. They named their technique steam-over-solvent injection in fractured reservoirs (SOS-FR).

SOS-FR method consists of three phases applied in the form of cyclic (huff-and-puff) injection:

- Phase 1: Steam or hot water is injected to heat the reservoir and to reduce the viscosity, oil recovery in this stage is mainly due to thermal expansion and gravity drainage.
- Phase 2: Solvent is then injected to further reduce the viscosity and to diffuse into matrix oil and produce the oil by gravity. In oil-wet systems such as carbonate reservoirs, capillary imbibition may also play a role if there is any water phase in the rock (entered into the core during Phase 1 by capillary imbibition or contraction of oil during the cooling period between Phases 1 and 2).
- Phase 3: Finally, hot water or steam is introduced to retrieve the solvent and recover additional oil.

The above described method suggests a “thermal” approach to retrieve the solvent. In other words, the solvent diffuse into matrix can be retrieved thermodynamically. Using refractometer index and weight difference methods, Al-Bahlani and Babadagli (2008) estimated solvent retrieval of about 85-90% at the end of the process. Note that accurate measurement of the solvent retrieved was not quite simple as the solvent used (heptane) was in vapor phase during its retrieval (**Figure1**) and therefore highly volatile. This makes us questions these two important issues:

- How can the retrieval solvent during Phase 3 (above) be accurately estimated?
- What are the ideal conditions (mainly the solvent type and corresponding optimal temperature) to maximize the solvent retrieval?

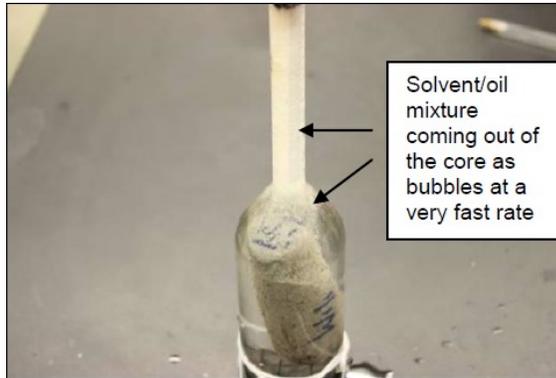


Figure 1: Solvent retrieval process by boiling at high temperature (Al-Bahlani and Babadagli 2008).

At the end of oil production period (after Phase 2 and even Phase 3 under certain circumstances), a considerable amount of solvent mixed with oil is remained locked in the matrix. This precious amount of diluted oil inside the matrix can be retrieved by water imbibition before or after Phase 3 if the wettability of the medium is altered to be water-wet. If proper wettability alteration chemicals are added to the hot-water phase (Phase 3 above), or even applied as cold water with these chemicals, one may be able to exchange the oil-solvent mixture in the matrix with the aqueous phase injected.

The crucial role of reservoir wettability on primary oil recovery methods such as water drive was recognized by early research (Bobek et al., 1958). Secondary recovery by waterflooding is directly related to wettability of oil reservoir, as well. Wanger and Leach (1959), for example, stated that oil recovery during water flooding for an oil-wet reservoir can be less by 15% in comparison with water-wet reservoir. EOR process may change the crude oil/brine/rock properties by two mechanisms: Coating and cleaning (Giraldo et al., 2013). Coating refers to the process of covering the oil-wet layer by water-wet materials. For example, zirconium nanoparticles are hydrophilic and when they adsorb on the rock surface and form nanotexture, coating the oil-wet surfaces (Karimi et al., 2012a), wettability changes to more water-wet. Cleaning mechanism is normally associated with surfactant-induced wettability alteration. Cationic surfactants, for instance, desorb the oil-wet layer and thus render the surface more water-wet (Standnes and Austad, 2000). In addition to surfactants and nanofluid, there are many other chemicals that can adjust the physiochemical properties of the matrix, such as: High pH solution, low/high salinity water, and ionic liquids. Determining the potentially feasible chemicals in each reservoir is an essentiality unique process and proper approach to select and optimize the use of these chemicals is, no doubt, of great importance.

Aims and Objectives

This research aims to perform the following objectives:

1. To design an experimental setup for measuring the retrieved solvent amount during SOS-FR.
2. To optimize the most critical parameters affecting the SOS-FR process study of:
 - Solvent type
 - Solvent soaking period
 - Cycle numbers and durations
 - Temperature during Phase 3
3. Repeating these optimization tests for different parameters such as:
 - Rock properties (wettability and permeability)
 - Oil viscosity
 - Boundary conditions
4. To fill the gap in the area of wettability alteration processes by summarizing and critically analyzing materials/methods mostly suggested for light oil systems in the literature.
5. To examine the potential wettability alteration chemicals as listed below and processes selected through this literature review to be used for heavy oil containing NFCRs:
 - Surfactants
 - High pH solution
 - Low and high salinity water
 - Nanofluids
 - Ionic Liquids
6. To clarify the effect of solvent dilution-retrieval process on the wettability of heavy oil containing oil-wet systems.

Structure of the thesis

This is a paper-based thesis and is composed of five chapters. The main body is constructed from 3 papers that have been submitted or prepared for peer-reviewed journals. Versions of Chapter 1 and Chapters 3 were presented at two conferences. Chapters 2 to 4 contain its own introduction, literature survey, results, conclusions, and references.

Chapter 1

This chapter provides an introduction to the thesis and an overview. Then, a brief background about solvent retrieval and wettability alteration are discussed. Following that, it highlights the statement of problem, major objectives, and goals.

Chapter 2

A new experimental setup was designed to quantify the solvent retrieval during hot-water phase of the Steam-Over-Solvent in Fractured Reservoir (SOS-FR) method. A detailed clarification study on the effect of different factors on this process is provided using core scale experimentation. Conditions to improve the efficiency of solvent retrieval were determined including the optimum solvent type, soaking periods, and hot-water temperature, etc.

Chapter 3

Solvent retrieval in Chapter 2 was performed using hot-water at high temperature. Non-thermal methods that can be applied to retrieve the solvent require the wettability alteration of oil-wet systems. A comprehensive review study is presented to explore the possibility of wettability alteration of heavy oil containing oil-wet system. Both materials and methods are discussed. This chapter concludes with a list of the most promising potential wettability modifiers for each type of rock system

Chapter 4

This chapter experimentally examines the wettability alteration agents suggested in Chapter 3. Experiments were performed using a new approach composed of two stages. Two types of solvent were investigated. Solvent retrieval and oil recovery were assessed for different sets of solvent type/rock characteristics and wettability modifiers. Best phase sequence and wettability modifiers for sandstone and limestone are identified. New type of chemical solutions alters the wettability of sandstone and limestone.

Chapter 5

The last chapter contains the contributions and achievements of this thesis and provides recommendations and suggestion for future work.

CHAPTER 2: EFFICIENCY OF SOLVENT RETRIEVAL DURING STEAM-OVER-SOLVENT INJECTION IN FRACTURED RESERVOIRS (SOS-FR) METHOD: CORE SCALE EXPERIMENTATION

This paper is a modified and improved version of SPE 165538, which was presented at the SPE Conference held in Calgary, Alberta, Canada, 11–13 June 2013. A version of this chapter has been submitted to the Journal of Canadian Petroleum Technology.

Preface

Sole injection of steam or solvent into heterogeneous reservoirs usually yields an inefficient recovery performance. The SOS-FR (Steam-Over-Solvent Injection in Fractured Reservoirs) method was suggested as a solution to improve the efficiency of heavy-oil/bitumen recovery from fractured carbonates and oil sands reservoirs after cold production (Al-Bahlani and Babadagli 2008). The method consists of three phases: Phase (1): Steam is injected at low temperatures to heat the matrix and condition the oil for subsequent solvent injection; Phase (2): solvent injection to dilute matrix oil by diffusion and enhance gravity drainage recovery rate, and; Phase (3): low temperature (around the boiling point of solvent) steam injection to retrieve the solvent diffused into matrix.

Previously, we focused on the effectiveness of Phases (1) and (2) of the method (Al-Bahlani and Babadagli 2009a-b) and observed very positive responses at the field scale (Al-Bahlani and Babadagli 2010) with high ultimate recoveries. The efficiency of this process, however, is purely determined by the amount of solvent retrieved at the end of the process. This paper, therefore, focuses on Phase (3), which is done mainly for solvent retrieval.

Twenty two static core experiments were performed on water and oil-wet sandstone and limestone. After saturating the rock samples with different heavy-oils, they were immersed into different liquid solvents—hexane, heptane, decane, and diluent oil. Once the ultimate recovery was achieved by diffusion and gravity drainage [Phase (2)], the samples were exposed to different temperature hot-water [Phase (3)] and the amount of solvent retrieved was measured through volumetric and weight measurements, as well as refractometer readings. The retrieval of solvent diffused into matrix was mainly due to two reasons: (1) Evaporation of solvent at elevated temperature, and (2) imbibition of hot-water into rock (if oil-wet samples become more water-wet during Phase (2)).

The amount of solvent retrieved through these processes were determined and the efficiencies were analyzed for different parameters including rock wettability, oil viscosity, solvent type, solvent-soaking period, rock type, boundary conditions, and different combinations of steam-solvent cycle, and temperature applied.

1. Introduction

Thermal enhanced oil recovery methods (mostly steam injection) have been widely used to recover heavy-oil from sandstone reservoirs. Different versions of hybrid thermal-solvent recovery methods have also been proposed in literature to increase the efficiency of heavy-oil recovery by reducing the amount of steam used. For example, solvent injected with steam can help to minimize the required energy during steam assisted gravity drainage (SAGD) process (Li et al. 2011a-b; Nasr et al. 2003), while the combination of solvent and steam injection is suggested to benefit from the wormholes created after Cold Heavy Oil Process Sand (CHOPS) (Rangriz-Shokri and Babadagli 2012a-b). When solvent is used solely or in combination with a thermal method, the main challenge is to retrieve the injected solvent due to its high cost. This means the feasibility of any hybrid or sole solvent injection method relies on two factors: oil recovery and solvent retrieval.

However, these processes usually are not easily applicable for naturally fractured carbonate reservoirs, where most of the oil is stored in matrix and the fracture network only controls the flow. Recently, Al-Bahlani and Babadagli (2008) developed a new approach named SOS-FR (steam-over-solvent injection in fractured reservoirs) to recover matrix oil in naturally fractured reservoirs.

The SOS-FR method consists of three phases:

- Phase (1): Steam or hot water is injected to heat the reservoir and reduce the viscosity. Oil recovery at this stage is mainly due to thermal expansion and gravity drainage if the matrix does not show any affinity to water to yield capillary imbibition.
- Phase (2): Solvent is injected to further reduce the viscosity by diffusing into matrix oil and produce the oil mainly by gravity. In strongly oil-wet systems such as carbonate reservoirs, capillary imbibition may also play a role if there is any water phase in the rock, which enters into the core during Phase (1) by capillary imbibition or contraction of oil during the cooling period between Phases (1) and (2).
- Phase (3): Hot water or steam is introduced to retrieve the solvent and recover additional amount of oil.

Using refractometer index and weight difference methods, Al-Bahlani and Babadagli (2008) estimated solvent retrieval of about 85-90% at the end of the process. However, this measurement was not a simple exercise as the solvent used (heptane) was in vapor phase during its retrieval and therefore highly volatile. Measuring the retrieved solvent amount is an essential step for optimizing the SOS-FR method. Quantifying the produced solvent at the end of the SOS-FR

method is a very critical step in the viability of this method. It also has a direct impact on the other related solvent based processes, such as ES- SAGD and post-CHOPS recovery methods by solvent.

This work focuses on quantifying the solvent retrieved during Phase (3) of the SOS-FR process, and to investigate the effect of different parameters on the process such as:

- a) Wettability of the rock
- b) Oil viscosity
- c) Temperature of steam/hot water during Phase-3 (solvent retrieval phase)
- d) Solvent type (different molecular weights and boiling points)
- e) Cycle numbers and durations (injection, soaking and production). Two different cycle types were tested:
 - Solvent soak-production / solvent soak-production .../ and hot water.
 - Solvent soak-production-hot water / solvent soak-production-hot water/
- f) Rock type
- g) Boundary conditions

2. Methodology

The experiments were conducted using Berea sandstone ($\phi=19-21\%$, $k=100-200\text{md}$) and limestone ($\phi=12-15\%$, $k=1-6\text{md}$) core samples obtained from the same outcrop block. The cores were 1.5 inches in diameter and 3.5 inches in length. Before the saturation process, the wettability for oil-wet core samples was altered using two ways. The wettability of the sandstone cores was altered to oil-wet using Surfasil™ following the procedure described by Al-Bahlani and Babadagli (2008). This process was performed in three steps: (1) Cores to be treated were saturated with a mixture of 10% Surfasil™ and 90% toluene, (2) the cores were saturated with toluene to displace any excess Surfasil™, and (3) the cores were saturated with methanol to preserve continuous oil wetness. The samples were then left to dry for 24 hours. After that, the wetting angles for the cores were measured and found to be more than 90°C , confirming the wettability alteration. The wettability of one Berea sandstone core was modified by aging the core plug under vacuum for 6 weeks at 50°C . Wettability alteration was assured by contact angle measurements.

As heavy-oil, a crude sample with a viscosity of 1,730 cp was used for most of the experiments (type A). One Berea sandstone core was saturated with a 14,000cp oil (type B). Table 1 provides the density and the viscosity values for both oil types. The saturation of the core samples was performed under vacuum in an oven (to heat the oil and ease the saturation) for five days. The weight of the cores was measured before and after the saturation and the volume of oil in place

was then calculated.

As the main objective of this paper was Phase(3) of the SOS-FR process, i.e., solvent retrieval, the first phase was skipped in all experiments; hence, the experiments started with Phase (2), which is solvent exposure, and oil recovery was calculated measuring refractometer indices and weight change. Next, to observe the contribution of capillary imbibition in total recovery, the cores were immersed into water at room temperature at the beginning of Phase (3) and then put in an oven at a constant temperature to retrieve the solvent. The oven temperature was then set at the desired temperature to retrieve the solvent by boiling it. These two steps, capillary imbibition at room temperature followed by hot water injection at a temperature near to the boiling point of the solvent, would remove the solvent from the core.

3. Experimental Design and Setup

Twenty two experiments were performed using different wettability cores samples. For Phase (2), four different types of solvents were used. To find the optimum combination of soaking periods and cycle types, different cycle numbers and durations were tested. In four experiments the temperature at Phase(3) was set to be lower and higher than the base case temperature which was set to be 90°C. The solvent recovery and oil recovery at the end of each experiment were given as percentage of the pore volume (or original-oil-in-place as there is no initial water in the system). Table 2 gives a summary of the experiments.

To compare the results of different cases, the key measurement indicators for each case were oil recovery and solvent retrieval. Al-Bahlani and Babadagli (2009) attributed the difficulty in quantifying the solvent retrieval to the high volatility of solvent in its gaseous phase. To overcome this challenge, different experimental setups were tested. It was found that the condensation of the retrieved solvent was the best method to quantify the amount of solvent retrieved at the end of Phase (3). **Figure 1** shows the suggested experimental set up, which consists of an imbibition cell placed inside an oven and connected to a graduated cylinder outside the oven kept at a lower temperature. The described design provides mean to quantify the solvent retrieved during Phase (3) accurately.

4. Description of Experiments and the Critical Parameters Tested

As mentioned above, several critical parameters affecting solvent retrieval during Phase 3 (and oil recovery during Phase 2) were tested and are described below. To test the effect of the wettability on the solvent retrieval during Phase (3) of the SOS- FR method, four core samples with different wettabilities were used. A water-wet (core #7), an oil-wet (core #23), an aged sandstone (core #17)

and a limestone (core #22) core sample were immersed into solvent for about 10 days. The refractive index readings were taken periodically and indicated the highest oil production from the oil-wet sample as will be discussed later.

After Phase (2), the core samples were immersed into water and put in an oven. The temperature of the oven was increased gradually to 90°C, which is a temperature very close to the boiling point of heptane and was taken as the “base temperature”. No oil was produced during the early time of this period, neither from the oil-wet sandstone nor limestone as no capillary imbibition took place. As opposed to this, a considerable amount of the oil recovery was obtained during this period from the water-wet core.

When the water temperature became high enough, the oil production was observed from all core samples, which can be attributed to thermal expansion. The oil recoveries during this period were in the range of 19-21%OOIP. Al-Bahlani and Babadagli (2008) reported that the oil production by thermal expansion at 90°C from an oil-wet sandstone is around ~10%, which is lower than our observations. Hence, the incremental oil recovery can be also attributed to the pushing force of solvent by its boiling and possibly capillary imbibition occurred by a degree of wettability change and reduced viscosity of oil due to solvent dilution. The experiments did not last long enough to observe any of the effect of the gravity drainage on oil recovery.

Effect of oil viscosity on the process was investigated by running one experiment using another oil (type B) which has a viscosity of 14,000 cp at 25 °C (Table 1). Core #15 was saturated with this oil and then Phase (2) of the process was applied. Soaking period was 2.5 days; Phase (3) was run under 90 °C.

To study the effect of the solvent type on solvent retrieval, we immersed four different oil-wet core samples into four different solvents (hexane, heptane, decane and diluent oil). The refractive index readings were used to estimate the oil recovery during this phase. The cores immersed into hexane and diluent oil had a darker color over time which indicates a better mixing even though they had slower diffusion rates than the lighter solvents. After about 2.5 days, the cores were taken out of the solvent. **Figure 2** shows the imbibition cell with core #2 and during Phase (2). **Figure 3** illustrates the asphaltene precipitation at the surface of the core after Phase (2). The final refractive indices were taken together with the weight after Phase (2) to estimate the oil production and the amount of solvent diffused into the core. Phase (3) was then applied immediately by putting the cores into the oven. The temperature of the oven was increased gradually to 90 °C in the case of heptane, decane and diluent oil, and to 70°C for the hexane.

No oil recovery was noticed at the beginning of Phase (2) (while the core was heated) indicating that the wettability of the core samples had been altered successfully to oil-wet. As the temperature of the medium was increased, the oil bubbles started to appear in the upper part of the imbibition cells (**Figure 4-a**). Oil production during this period was attributed mainly to thermal expansion. After about one hour, solvent bubbles were seen coming out of the core sample which had been immersed into heptane, hexane and diluent oil. **Figure 4-b** shows a big solvent bubble coming out of the core sample during Phase (3). No bubbles were seen in the case with decane as the temperature was not sufficient to reach the boiling point of decane. **Figure 4-c** shows the oil production at later times of Phase (3).

While the solvent vapor pressure was increasing, the solvent bubbles started leaving the core towards the upper part of the imbibition cell and flowing through the connecting tube out of the oven. **Figure 5** illustrates the solvent retrieved during Phase (3). As the solvent vapor moved out of the core, it condensed and flowed towards the graduated cylinder outside the oven. To avoid any loss of solvent, the graduated cylinder was kept at low temperature using ice. It is worth mentioning that solvent retrieval was quite fast and completed after the second hour of the process. Some additional oil was produced due to the pushing force of solvent bubbles as they were leaving the core samples.

Two Berea sandstone sample were soaked into heptane for 2.5 days. The oil recovery and the amount of solvent diffused into cores during this time were estimated using refractometer analysis. Each sample was then exposed to different hot water temperature for Phase (3). Core #6 was put in 85°C, which is about 5 °C less than the base case (core # 13, which was at 90°C). The temperature of the medium for core #10 was 96°C.

Different cycle types were tested against the base case (core sample #13), which was soaked into heptane for 2.5 days before applying Phase 3. Core #11 was first soaked into heptane for 1.25 days and the oil recovery during this period was estimated using refractometer analysis. Heptane was then replenished and the core was put into the solvent for another day. Finally, the core was immersed into water and it put into the oven where the temperature was increased gradually to 90°C. To test the effect of the third soaking period after Phase (3), a similar cycle was repeated for core#14, but this was performed after Phase (3). Then, the core was put immediately into the solvent for a 4-days soaking period before running Phase (3) one more time.

For core #5, a cycle of Phase (2) for 1.25 days and then Phase (3) were applied. In other words, a cycle of Phase (2)-Phase (3) was repeated twice. The oil recovery and solvent retrieval during this period was estimated using refractometer analysis and weight difference method. To test the effect

of the solvent soaking period, core#9 was soaked into heptane for 4.5 days. Soaking periods for core#4 and #16 were 5.5 and 60 days, respectively. The soaking period for the base case#13 was 2.5 days soaking period.

After performing sandstone experiments, two critical factors were identified to be tested using limestone: Soaking period and temperature during Phase (3). Three limestone samples were immersed into heptane for different soaking periods. Core#18 was soaked into heptane for 2.5 days. Soaking periods for core#24 was 6 days. Two experiments were added to clarify the efficiency of solvent retrieval in limestone at two different temperatures. Phase (3) of core #19 was run at 96°C while the Phase (3) temperature of core #18 was 90°C. Core#20 and core#21 were used to test effect of boundary condition. They were epoxy coated to generate counter-current type interaction and soaked into heptane for 55 days before applying Phase (3) at 90°C.

5. Results and Analysis

The interaction between oil-solvent-water in porous media is a complex process and becomes even more complex when this interaction takes place at non-isothermal conditions. One objective of this research was to understand how this ‘rock-fluids’ interaction affects the solvent retrieval during the SOS-FR method.

To calculate the oil recovery and solvent retrieved during the experiments, several assumptions were made. When a core was soaked into solvent for the first time, solvent diffused into porous media was assumed to be as much as the oil produced during this phase. Accordingly, the solvent retrieved in Phase (3) was given as a percentage of solvent diffused in Phase (2). After Phase (3), the cores were left to dry and the estimation of the final oil recovery from Phases (2) and (3) was based on the weight difference calculations, with an assumption that the amount of the water and solvent left in the cores is negligible (Naderi and Babadagli 2012). It should be noted that the soaking periods for most of experiments were chosen to be short (2.5 days) to avoid the effect of asphaltene on the refractive index readings. However, in longer soaking period time experiments, asphaltene precipitation in the produced oil or in the core surfaces affected the recovery calculations. In this case the results were integrated by the weight difference calculation method and the oil recovery during phase (3) was calculated using the following approach:

$$\text{Oil recovery during phase (3)} = \text{Final recovery} - \text{oil recovery during phase (2)}$$

Note that no solvent was assumed to remain in the cores and the collected oil after phase (3) in this exercise.

5.1 Effect of the wettability. Miscible fluids interaction is dominated by diffusion which is independent of surface characteristics. However, in porous medium this interaction occurs in micro channels and it is likely to be affected by the existence of transient /effective interfacial tension which was observed by many researchers (Joseph, 1991; Pojman et al., 2006). The existence of such an interfacial tension, even if it vanishes with time, can cause a capillary imbibition (Korteweg, 1901). This is expected in the early periods of solvent exposure of heavy-oil saturated oil-wet porous medium before relatively slower diffusion process starts to dominate the process. Al-Bahlani and Babadagli (2008) observed that oil-wet medium responds more positively to solvent phase during the SOS-FR process, which could be attributed to capillary imbibition of solvent due to oil-wet nature of the medium before the diffusion process dominates the process.

Similar observations were made by other in earlier studies. For example, Maini et al. (1986) demonstrated that oil-wet core would produce higher recovery compared to the water-wet cores when miscible flooding is performed at low injection rates. In a more recent work, Rezaei et al. (2010) observed a better performance of oil-wet medium over water-wet medium when they injected heptane in a VAPEX process. Also, a micro model study by Dehghan et al. (2009) showed that displacement of oil by solvent in water-wet medium is more efficient than in oil-wet medium in the presence of connate water.

All these observations indicate that the wettability could be a critical factor in the interaction of two miscible phases, especially in the case of diffusion dominated heavy-oil displacement processes. Therefore, different wettability samples were tested under the same conditions. Four different wettability core samples were assessed firstly based on final oil recovery factors calculated using weight difference. **Figure 6** shows that water-wet core gave the highest oil recovery of about 82 % OOIP. The oil-wet core had a slightly lower recovery of about 79% OOIP. The limestone and the aged core gave the lowest recoveries of 72% OOIP and 67% OOIP respectively. Al-Bahlani and Babadagli (2008) reported similar trends of oil recoveries when they compared oil and water- wet cores even though they applied a hot/water phase before the solvent phase.

The two shown in Figure 7 should be analyzed separately. In phase (2), the oil-wet sandstone yielded the highest recovery among all confirming the possible contribution of “capillary imbibition” of solvent to the process as discussed above. That is to say, solvent intrusion into the sample took place by capillary suction at early stage of the experiment due to strong oil wetness before the diffusion dominated mixing process initiated. Water-wet and aged cases yielded almost the same recovery during this phase. As the system is not as strongly oil-wet in the aged core case

as the “oil-wet” case which underwent Surfasil treatment, no capillary imbibition is expected to occur. The lower recovery from limestone in phase (2) can be attributed to much lower permeability compared to the sandstone cases.

During Phase (3), water-wet sample yielded the highest recovery as expected. Capillary imbibition into the core enhanced by temperature effect took place and due to water-wet nature of the core 27% additional oil was recovered. This amount was limited to ~20 % OOIP for the oil-wet and aged samples. At this temperature (90° C), thermal expansion is expected to contribute up to 10 % OOIP. Additional 10% oil recovery in the oil-wet and aged sandstone and limestone cases can be attributed to pushing out of oil due to the boiling force of the evaporating solvent expecting no capillary imbibition of hot-water. The rest of the recovery (7%) in the case of water-wet sandstone is due to capillary imbibition. As mentioned earlier, the duration of the experiments was kept short (typically 3 hours) and the gravity effect is not expected to be critical on the recovery.

Solvent retrieval is a critical part of the SOS-FR method. **Figure 7** demonstrates that a high percentage of solvent (90-95%) was retrieved in all cases. This amount justifies the economic and technical feasibility of the method. The solvent retrieval amounts are slightly higher than what was observed by Al-Bahlani and Babadagli (2008) in their initial attempts. This is obviously due to reliability of the solvent capture system developed in this paper (Figure 1), which is a purely close system and solvent loss during liquefaction of vapor solvent is nil.

As a final point, it should be emphasized that wettability plays a critical role during this process. Although the difference is not critically high, the oil-wet case yielded the lowest solvent retrieval compared to the others. This is an indication of wettability and oil-wet sample retained more solvent (or hydrocarbon phase) in the system during Phase (3). Once again, this is not a critical amount in terms of the feasibility of the method but this observation is useful in identifying the role of wettability on the physics of the process. Eventually, ~95% solvent retrieval by boiling it in a short period of time, regardless wettability, is sufficient to justify the feasibility of the method.

5.2 Effect of oil viscosity. A lower grade oil (higher oil density and viscosity) was used to saturate core # 15 (Table 2). The soaking period was 2.5 days as similar to the core # 13 which was base case. **Figure 8** shows that oil recovery reduction due to the more viscous nature of the oil was mild (about 3%). The solvent retrieval, however, was about 20 % less than the base case (**Figure 9**). Note that solvent retrieval is a quick process (order of 120 minutes) and draining 14,000cp oil mixed with solvent by gravity and capillary imbibition takes much longer time

compared to the case with 1,730 cp oil. Hence, the solvent retrieval of 50% is due only to boiling effect with minimal contribution of capillary imbibition and gravity drainage

5.3 Effect of temperature during Phase (3). The main mechanism of solvent retrieval during Phase (3) is the vaporization of solvent at higher temperature (boiling). To minimize the cost of the process, temperature (steam or hot water injection) during Phase (3) should be maintained at minimal levels. We investigated the effect of the temperature at Phase (3) by applying three different temperatures on three different cores. As mentioned before, the base case temperature was 90°C and most of the experiments were performed at this temperature. The temperature was set to be slightly lower for one case (85 °C for core #6) and a higher temperature was also applied to retrieve the solvent from core #10. As shown in **Figure 10**, it is clear that hot water temperature at Phase (3) has a profound effect on solvent retrieval even though the temperature range is very narrow. A small drop in temperature from 90 °C to 85 °C caused a significant fall in solvent retrieval; from 72 % to 10 %. When hot water temperature is around 96 °C, which is very close to the boiling point of heptane (98 °C) at atmospheric pressure, the solvent recovery went up to 85% of the solvent diffused into core during Phase (2). It was also observed that not only a higher solvent recovery could be achieved at higher temperatures but also the total time required to reach the ultimate solvent recovery was shorter.

5.4 Effect of solvent type. One of the critical factors in this kind of thermal-solvent hybrid process (like the SOS-FR method) is to select the proper solvent. Al-Bahlani and Babadagli (2009a) showed that the lower the solvent carbon number, the higher diffusion rate is. Although this accelerates the recovery process, the ultimate recovery is lower due to less effective mixing (Coskuner et al. 2013;Naderi et al. 2013) and more asphaltene precipitated (Arciniegas and Babadagli 2013). Hence, a wide range of carbon number solvents were tested. **Figure 11** shows the effect of solvent type on oil production during Phase (2).It is obvious that core #2 exposed to hexane, and core #3 exposed to diluent oil, produced the highest amount of oil (~45 % OOIP). Core #13, which represents the base case, recovered about 36 % OOIP. With an oil recovery of about 26 %, the core sample #8 (decane case) had the lowest oil recovery. Note that these recoveries are relatively lower than observed in the previous studies (Al-Bahlani and Babadagli 2008, 2009a;Coskuner et al. 2013;Naderi et al. 2013). This is mainly due to shorter solvent exposure times applied in the present study, which did not allow sufficient time to produce more oil by gravity drainage. As the main objective of this work was to assess the solvent retrieval, solvent exposure times were limited to several days compared to the earlier studies above referenced, which were conducted over weeks.

The performance of diluent oil (carbon number in the range of C11-C13) is interestingly high. This was attributed to the existing aromatic groups within that dissolve heavy-ends of crude (Coskuner et al. 2013; Naderi et al. 2013), which does not exist in single-component alkane type solvents. As expected, the diffusion rate of decane was smaller than other alkanes (hexane and heptane) and more time was needed to recover heavy-oil.

In terms of solvent retrieval, **Figure 12** illustrates that about 72 % of heptane and diluent oil was retrieved after 2.5 soaking period. The hexane retrieval was much less with about 47 %. Obviously, hexane's boiling point is much lower than heptane but the solvent retrieval is lower. This brings up another question on the existence of an optimal temperature in solvent retrieval, which is currently under further investigation. No decane was retrieved at 90°C; this was expected as the boiling point of decane is far higher than this temperature (174°C).

5.5 Effect of cycle type. In addition to solvent injection (one cycle only) followed by Phase (3), we tested two other scenarios: (1) The solvent was replenished mimicking cyclic injection of solvent periodically before only one run of Phase (3), and (2) each solvent cycle (Phase 2) was followed by Phase(3). **Figure13** illustrates the effect of cycle type on oil recovery. When the results from different cycles are compared, one can see that a core #5 achieved the highest recovery (46% OOIP) with a slight improvement over core #14 (45%). Core #11 had 42 %OOIP recovery while the lowest recovery was obtained for core #13, which represents the base case of SOS-FR process with about 36 % of OOIP.

It is obvious that cyclic solvent stimulation followed by a single run of Phase (3) had a better performance than single run of Phases (2) and (3). Al-Bahlani and Babadagli (2009) observed a similar design to be more economical at the field scale through their numerical runs. Recent optimization studies showed that this type of cyclic injection of solvent (Phase 2 up to 12 cycles at the field conditions) also gave similar results (Al-Gosayir et al. 2013).

In all cases, the replenishment of solvents led to a more efficient process than the base case [single run of Phases (2) and (3)]. The results also revealed that the best cycle performance in terms of oil recovery was achieved by a repetition of cycles of Phases (2) and (3) (core #5). This produced about 5% OOIP more than multiple cycles of Phase (2) followed by Phase (3) (core #11). This difference can be explained as follows: In the cycle type of [Phase (2)-Phase(2) and Phase(3)], the replenished solvent around the core diffused into the outer region of the core and mixed with oil which already had a high concentration of solvent from the first cycle. Essentially less efficient diffusion took place in this case than it would have if the solvent contacted the inner surfaces of the core that had a higher oil concentration. This was not the case in the other configuration [Phase

(2)-Phase (3)-Phase (2)-Phase (3)]. The oil expanded during Phase (3) right after the first cycle of Phase 2 to the outer surfaces of the core and was produced partially during this phase. Then, the concentration of oil in the outer region became higher. When the temperature reached the boiling point of solvent, it started boiling and leaving the core. In the course of Phase (2) of the process, the solvent diffused to the outer surfaces of the core, which in this time, had more oil concentration and hence more efficient diffusion was achieved. Another reason for the improvement in oil recovery in this cycle could be attributed to capillary imbibition during Phase (3) cycles. The system may become more water-wet as the oil is diluted with solvent during Phase (2) cycles and some amount of water may enter the core by capillary imbibition expelling additional oil and solvent.

In the case of core #14, the soaking period after Phase (3) lasted for 4 days and then Phase (3) was applied. Oil recovery increased to slightly exceed the best case scenario (core#5). The mild difference in oil recovery, in spite of longer soaking period, indicates the importance of the optimization on the process (from cycle durations and number of cycles point of view). If a considerable amount of water is intruded into the system (due to oil contraction or capillary imbibition if oil-wet samples become more water-wet), the diffusion process in the subsequent cycles might be affected negatively. Hence, one may conclude that the duration and number of Phase (3) in cyclic solvent stimulation processes can also be an important optimization factor as it has a critical impact not only on solvent retrieval but also the diffusion of solvent in the subsequent solvent cycles.

It was possible to retrieve about 86% of the solvent diffused into core #11 when we applied two cycles of Phase (2) followed by Phase (3). However, it was difficult to determine the exact amount of solvent retrieved as a fraction of the total amount of solvent diffused into the cores in the cyclic solvent cases (core #5 and #14) with more than Phase (3) runs in between compared to single solvent cycle case. This difficulty is due to the solvent replaced by water that penetrated into the core in the previous cycles of Phase (3) assuming that a degree of wettability alteration took place after solvent treatment during Phase 2. This makes it difficult to determine the initial solvent in the core before starting Phase (3). Eventually, refractive index was used to estimate the amount of solvent retrieved from core #5 and core #14, which lied in the range of (75-85%).

5.6 Effect of soaking period. To study the effect of soaking period during Phase (2), three cores sample were put into heptane for 2.5, 4.5 and 5.5 days. As seen in **Figure 14**, core #4 which was soaked into solvent for the longest period and produced about 55% OOIP, which is about 10% higher than that of core #9, which was immersed in heptane for 4.5 days. The oil recovery from core #13, which was soaked into heptane for 2.5 days, was about 36 %OOIP. It is clear that the

longer the soaking period, the higher the oil recovery. The solvent retrieval followed a similar trend (**Figure 15**). One may observe that the solvent recovery jumps from 72% for the case of 2.5 soaking period to about 90% OOIP for the case where the soaking period was 5.5 days. Core # 16 was soaked into heptane for 60 days. The measurement of refractive index at the end of this period was unreliable due to the high amount of asphaltene precipitation. As a result, accurate estimation of oil recovery during Phase(2) was difficult, however, the weight difference indicated about 85%OOIP final recovery which was the highest oil recovery among all cores. The solvent retrieval for this core was expected to be in range of (83% -96%). These figures were estimated by assuming (10-20% OOIP) oil recovery during Phase (3). In spite of being a slow process, diffusion could result a significant amount of oil being recovered over time.

5.7 Effect of rock type. Two different rock samples used in this study exhibit different pore structures, permeability, wettability, and thus respond differently to the different phases of the SOS-FR method. As noted earlier, SOS-FR process is governed by the efficiency of solvent diffusion (Phase 2) and solvent retrieval (Phase 3). The soaking time during Phase (2) was identified to be an important factor. Temperature, on the other hand, is critical during Phase (3) as it directly affects the amount of solvent retrieved. These two factors were studied for different rock types.

5.7.1 Solvent diffusion process during Phase (2). **Figure16** compares oil production of three limestone core samples that were immersed in heptane for different soaking periods. Core#18, which was soaked for 2.5 days, produced about 31% OOIP. Increasing the soaking period to 6 days for core#24 resulted about 39 % OOIP oil recovery. Oil recovery for core# 22 went up to about 47% OOIP. The soaking period for this core was extended to 10 days. During Phase (3), the solvent retrieval exceeded 90% for all cases. As shown in **Figure 17**, it increased slightly from about 91% for core#18 to about 93% for core#24. Solvent retrieval reached 96 % for core# 22. In comparison with sandstones, limestone produced a relatively lower oil recovery. In **Figure 18**, another difference can be observed. Oil recovery during Phase (2) is faster for the sandstone case. As mentioned earlier, wettability of sandstones was changes to oil-wet. As the porosity was almost the same, the improvement in the performance of the sandstone was attributed to the effect of pore structure. Complex pore structure of limestone results low permeability. Consequently, the diffusion process is less efficient and less amount of solvent intruded into porous medium.

5.7.2 Solvent retrieval process during Phase (3). Two limestone core samples were immersed into heptane for the same period (2.5 days). Refractive index indicated that about 31% OOIP was recovered during this phase in both cases. This test confirms the repeatability of refractive index measurements. **Figure 19** shows that about 91 % of the diffused solvent was retrieved from

core#18 during Phase (3). The temperature was 90 °C. In core#19, temperature during Phase (3) was increased to 96 °C. As shown in **Figure 20**, solvent retrieval improved at this temperature to 98%. Once again, as noticed in sandstone, the solvent retrieval at temperature that was closer to solvent boiling point not just caused higher solvent retrieval, but also led to quiet faster process. The slight increase in oil recovery during Phase (3) for core#19 was attributed to the pushing force of boiling solvent. Comparison between solvent retrieval for sandstone and limestone at similar temperatures revealed that higher percentage of solvent can be retrieved in limestone (**Figure 21**). Note that amount of solvent diffused in the limestone cases is slightly less than that in the sandstones cases. As mentioned earlier, the diffusion process is negatively affected by the complex pore structure of limestone. It is possible that considerable amount of diffused solvent was not fully mixed with original oil in place. Thus, it was easy to retrieve this part of solvent leading to higher solvent recovery.

5.8 Effect of boundary condition. To represent a counter-current type fracture-matrix transfer, which is a commonly suggested interaction type in fractured reservoirs, limestone core sample# 20 and #21 were coated from all sides except one. The matrix-fracture interaction configurations for both core types are seen in **Figure 22**. Fracture interaction in core#20 is through the open end at the bottom (gravity drainage is possible) and it is through the open top part (against gravity) for core# 21. In other words, in terms of gravity, core#20 was the optimistic situation for recovery as the heavier oil moves down while the lighter oil mixed with solvent (or solvent alone) travels against gravity to the upper part, which is not an open end. Hence, for solvent retrieval it is an opposite situation and it is the most pessimistic case as solvent liberated from oil moves upward and accumulates at the “no-flow” top boundary instead of flowing down to be produced. Core #21 represents an opposite case.

The cores, representing these two extreme boundary conditions, were soaked into heptane for about 55 days. Refractive index readings indicated that about 10 % OOIP was recovered in both cases. Solvent diffusion was the main recovery mechanism in both cores with minimal effect of gravity due to “no-open” ends. Note that, oil was expected to be recovered in core #20 by gravity as well. The dark color at the bottom of the imbibition cell that contained core#20 indicates that produced oil accumulated close to the open-end likely in the form of asphaltene (**Figure 23**). As a result, both diffusion and gravity through the open end were suppressed even though the flow direction was in favor of gravity for oil production. As opposed to this, a more homogenous mixing was achieved in core #21. Produced oil moved down continuously and thus the upper surface was exposing to fresh solvent and so the diffusion process was enhanced. However, recovery was not high due to lack of gravity support in the case of core#21 and it is purely controlled by diffusion.

The importance of this observation is that it gives an idea of the limitation of long soaking period (asphaltene precipitation at the fracture surface) and due to matrix boundary conditions in fractured system for highly extreme (and pessimistic) conditions. After certain time, the accumulation of produced oil with heavy ends in fracture would lower the concentration difference and decrease the efficiency of solvent-oil diffusion process (core #20). During Phase (3), faster oil production was observed for core#21 which only had the top surface open. However, as shown in **Figure 24**, core#20 generated higher ultimate oil production during this phase, as expected.

The amount of solvent that diffused into porous medium was not very high (about 2-3 ml) in both cases. Because all the boundaries were closed except one, the boiling solvent was forced to go toward the bottom open surface pushing oil out of the matrix. Solvent settles at the top of cores because of gravity. When the temperature became closer to the bubble point of the solvent, solvent evaporated easily from core#21. Up to 60 % of the solvent was retrieved after about 5 hours as indicated in **Figure 25**. No solvent retrieved from core #20 during the first two hours, this was expected as the solvent boiling force had to exceed the gravity before solvent bubbles reaching the open bottom surface. As explained before, the pushing force of the solvent caused additional oil recovery during the solvent retrieval phase. Surprisingly, after six hours up to 47 % of solvent was retrieved from core #20 in spite of unfavorable boundary conditions. Note that the amount of retrieved solvent was very small (about 1.6 ml for core#21 and 1 ml for core#20). These two extreme boundary condition cases indicate that significantly longer soaking periods are required for an effective solvent diffusion. These periods may not be practically applicable (or tolerable) at the field scale.

6. Optimization of Oil Recovery and Solvent Retrieval during Phase (3)

As a result of solvent diffusion into a porous medium during Phase (2), a significant amount of oil can be produced by gravity driven by the dilution of oil. However, by the end of this phase, considerable amount of solvent will be left inside the matrix. During the early time of Phase (3), diluted oil (mixture of solvent and original oil) is produced because of the thermal expansion, gravity drainage and viscosity reduction. As temperature increases, solvent starts boiling and pushing oil out of the porous medium. The oil inside the matrix will become thick if the solvent is produced very fast by boiling it. As seen, this becomes an optimization problem that targets highest amount of oil recovery and solvent retrieval with minimized temperature and solvent use.

As shown in **Figure 26**, quantity of produced oil (accumulated at the upper part of imbibition cell)

decreases as solvent being extracted from both matrix and produced oil. The practical importance of this observation is that during Phase (3) of the process, water should be injected firstly at a temperature that is lower than the bubble point of the solvent.

While oil being produced at this stage, the temperature should be kept moderate until the ultimate oil recovery is reached and no oil is produced. Solvent retrieval should then be initiated to recover the -trapped- solvent in the matrix.

7. General Evaluation of the Results

Figure 27 compares the final oil production and solvent retrieval for all experiments. The uncertainty range in solvent retrieval due to measurement difficulties is indicated in the solvent retrieval values for cores #5, #14 and #16 using dotted lines. Heptane was used as a solvent in this study, except three cases (Table 2). Oil recovery factor in experiments that used heptane as a solvent was in range from 12% OOIP to 85%OOIP; the heptane retrieval was in range between 10% and 98%.

A reasonably high oil recovery (more than 60% OOIP) was achieved in sandstone experiments whenever the soaking period exceeded 5 days (core#4, #7, #16, #17, and #23). For the limestone cases, the needed soaking period to exceed the 60% oil recovery was about the double (i.e. 10 days, core#22). Note that the final recovery does not depend solely on oil recovery during Phase (2). The oil recovery during Phase (3) added a considerable amount of recovery in these cases, mainly due to the pushing force of boiling solvent. The associated solvent retrieval in mentioned cases was also good exceeding 80% of the diffused solvent. Solvent retrieval of this amount was achieved when the solvent phase was applied in a cyclic order (core#5 and #11) and temperature was very close to the boiling point of the solvent (core#10). On the contrary, solvent retrieval dropped far below this value when the temperature fell only 10 °C (core#6). Thus, small fluctuations in temperature around the boiling point of the solvent will have a great impact on solvent retrieval.

It is interesting to draw a comparison between the experiment with low temperature during Phase (3) (core#6) and experiments with sealed samples (unfavorable boundary conditions, core#20 and core#21) as they mainly represented the worst cases scenario for the process. In core#6, the soaking period was short (2.5 days), the amount of solvent diffused into the core was relatively small, therefore the solvent retrieval process during Phase (3) was not expected to contribute much to ultimate oil recovery. Hence, oil recovery was not affected significantly by lowering temperature during Phase (3). But, the solvent retrieval dropped dramatically to the lowest value

encountered in all experiments (10%).

Another factor affecting the recovery and solvent retrieval was matrix boundary condition. A dramatically low oil recovery values were obtained for the cases with unfavorable boundary conditions (12-16% OOIP). The coated core with only top side open (core#21) had the lowest oil recovery factor among all samples. Solvent retrieval was also low but not as dramatic as in the case of low temperature experiment (core#6).

The solvent retrieval performance in the limestone experiments (core#18, #19, #22 and #24) was superior to sandstone exceeding 80%. This can be attributed to the pore structure of limestones. As opposed to intergranular porosity system of sandstones, the vuggy nature of limestone may not cause entrapment of solvent, mainly in the form of gas, during Phase (3).

One may observe that cores#4, 7, 9, 16, 17, 23, and 24 yielded the highest recovery and highest solvent retrieval. This observation indicates that if the process is optimized for the duration of Phase (2) and temperature of Phase (3), and the proper solvent type is selected, the SOS-FR method can be applied efficiently regardless of the rock type (wettability and permeability).

8. Conclusions

A simple yet effective experimental setup was designed to quantify solvent retrieval during Phase (3) of SOS-FR method. The following observations were made out of this experimental study:

- The wettability the core samples did not affect the solvent retrieval process; on the other hand, temperature (Phase 3), solvent soaking time (Phase 2) and oil viscosity were the most critical factors affecting the amount of the solvent retrieved.
- Using the suggested experimental setup, it was found that the lower the hydrocarbon molecular weight, the higher the oil recovery.
- Diluent oil and heptane can be used as an effective solvent for Phase (2) of SOS-FR method with more than 70 % of solvent retrieval.
- A longer soaking period of solvent during Phase (2) would lead to a higher amount of solvent retrieval. The highest solvent retrieval was obtained from the cores immersed into solvent for 105.5 days with more than about 90% recovery factor. The solvent retrieval in the case of multiple cycles of Phase (2) followed by Phase (3) had slightly lower recovery of about 86% of the solvent retrieval.
- The closer the temperature to the boiling point of solvent, the higher amount of solvent can be retrieved in a shorter period of time; yet, a solvent can be retrieved in range of

temperatures below their boiling points. Temperatures below the boiling point of the solvent remarkably affected the solvent retrieval even if only by a few degrees (core #6 – heptane case). If it is substantially lower than the boiling point, no solvent was retrieved at all like in the case of decane used as solvent (core #8). However, diluent oil yielded reasonable good solvent retrieval at the same temperature even though its carbon number is higher than decane. This could be attributed to its better effectiveness in diluting oil during Phase (2) due to its aromatic content.

- Cyclical application of Phase (2) (injection of solvent, soaking period, and oil production) results in higher recovery than single cycle solvent injection. If this is applied in the form of [Phase (2)-Phase (3)-Phase (2)-Phase (3)], more oil recovery is obtained compared to Phase (2) cycles followed by a single cycle of Phase (3).
- Having a considerable amount of solvent diffused into the matrix, solvent retrieval process effectively enhanced the oil recovery through the pushing force of the boiling solvent during the solvent retrieval period (named as Phase 3).
- At range of temperatures close or around the bubble point of the solvent, solvent diffused can be retrieved even under unfavorable matrix boundary conditions.
- Before proceeding to solvent retrieval process by injecting water at the bubble point of the solvent, moderately hot water should be injected and all produced oil drained out of the fracture system. This may even contribute form capillary imbibition if expected wettability alteration due to solvent diffusion and mixing during Phase (2). Then higher temperature application may start to retrieve the great amount of solvent by boiling it.

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Table 1: Properties of type A and type B oil

Properties	Density (gm./ml.) at 25 °C	Viscosity (cp.) at 25 °C
Type A oil	0.9693	1730
Type B oil	0.9919	14000

Table 2: List of experiments

Core Number	Core type/ Wettability	Crude Oil Viscosity	Solvent Type	Soaking Periods	Temperature at Phase (3), °C
Core #2	Oil wet	1730cp	Hexane	Phase2(2.5days)-Phase3	90
Core #3	Oil wet	1730cp	Diluent Oil	Phase2(2.5days)-Phase3	90
Core #4	Oil wet	1730cp	Heptane	Phase2(5.5days)-Phase3	90
Core #5	Oil wet	1730cp	Heptane	Phase2(1.25days)-Phase3 - Phase2(1.25days)-Phase3	90
Core #6	Oil wet	1730cp	Heptane	Phase2(2.5days)-Phase3	85
Core #7	Water wet	1730cp	Heptane	Phase2(10days)-Phase3	90
Core #8	Oil wet	1730cp	Decane	Phase2(2.5days)-Phase3	90
Core #9	Oil wet	1730cp	Heptane	Phase2(4.5days)-Phase3	90
Core #10	Oil wet	1730cp	Heptane	Phase2(2.5days)-Phase3	96
Core #11	Oil wet	1730cp	Heptane	Phase2(1.25days)- Phase2(1.25day)-Phase3	90
Core #13	Oil wet	1730cp	Heptane	Phase2(2.5days)-Phase3	90
Core # 14	Oil wet	1730cp	Heptane	Phase2(1.25days)-Phase3 - Phase2(1.25days)-Phase3- Phase2(4days)-Phase3	90
Core #15	Oil wet	14000cp	Heptane	Phase2(2.5days)-Phase3	90
Core #16	Oil wet	1730cp	Heptane	Phase2(60days)-Phase3	90
Core #17	Aged	1730cp	Heptane	Phase2(10days)-Phase3	90
Core #18	Limestone	1730cp	Heptane	Phase2(2.5days)-Phase3	90
Core #19	Limestone	1730cp	Heptane	Phase2(2.5days)-Phase3	96
Core #20	Limestone(epoxy)	1730cp	Heptane	Phase2(55days)-Phase3	90
Core #21	Limestone(epoxy)	1730cp	Heptane	Phase2(55days)-Phase3	90
Core #22	Limestone	1730cp	Heptane	Phase2(10 days)-Phase3	90
Core #23	Oil wet	1730cp	Heptane	Phase2(10days)-Phase3	90
Core #24	Limestone	1730cp	Heptane	Phase2(6days)-Phase3	90

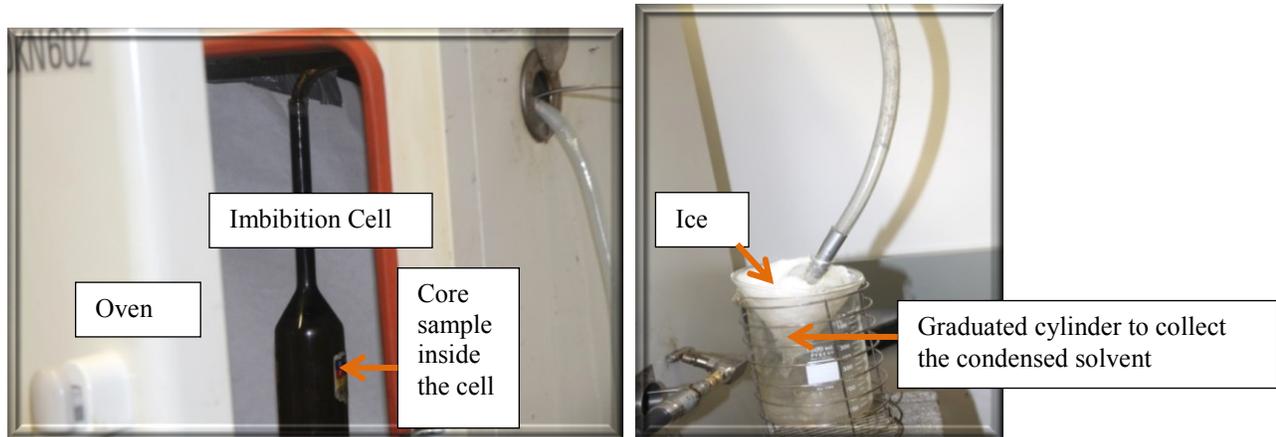


Figure 1: Suggested experimental setup for Phase (3) of the SOS-FR method.

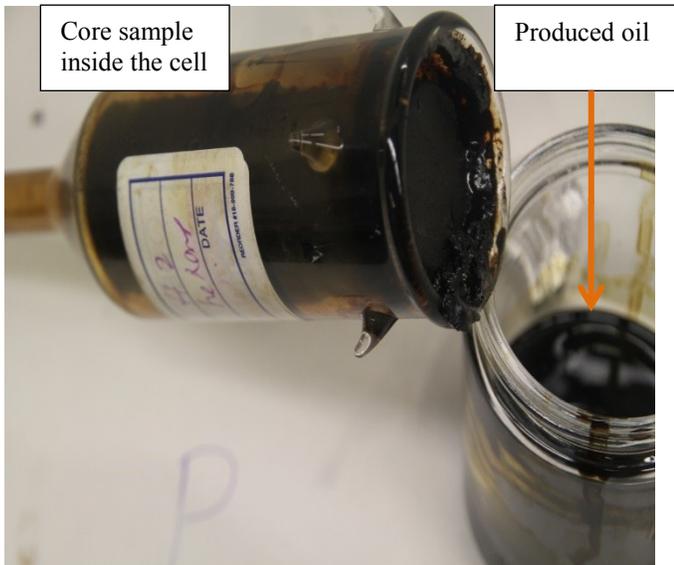


Figure 2: Imbibition cell which contained core #2 during the end of Phase (3).

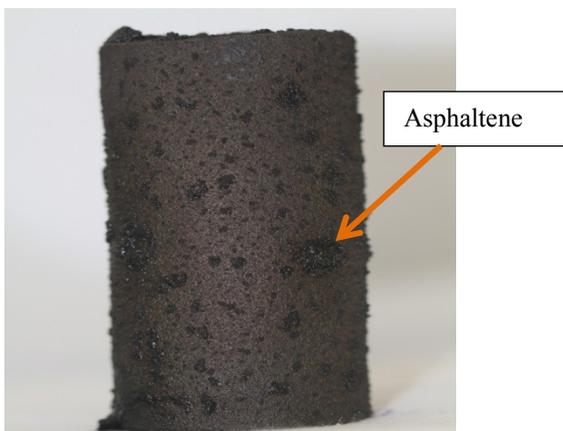


Figure 3: Asphaltene precipitation at the core surface at Solvent soaking period (Phase 2)



Figure (4-a)

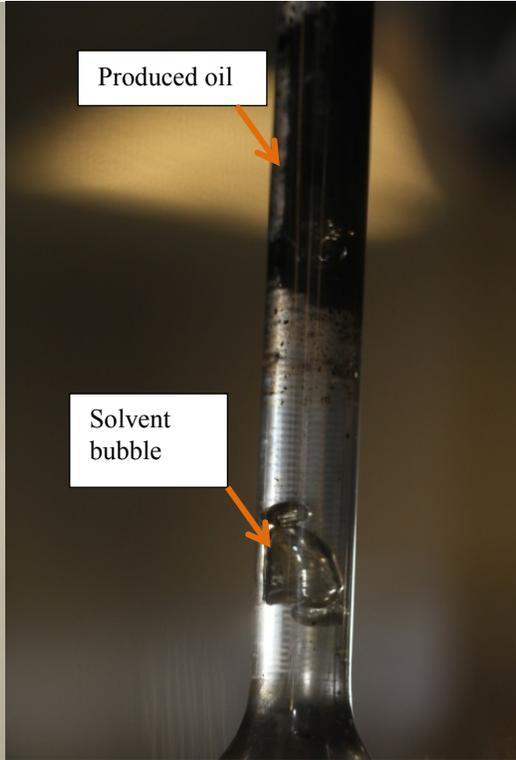


Figure (4-b)



Figure (4-c)

Figure 4: Phase (3) of the SOS-FR method for different experiments. (4-a): Oil production from core #3 at early time of Phase (3), (4-b): A big solvent bubble comes out of the core # 9 ,and (4-c): Oil production from core # 8 at later time.

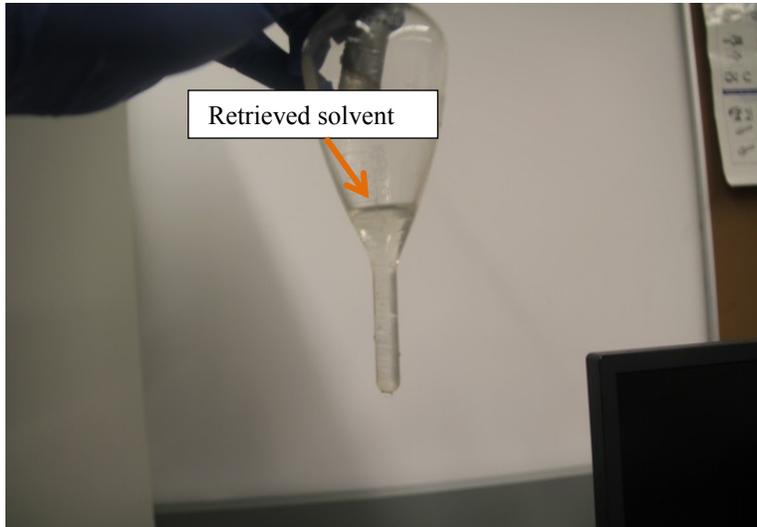


Figure 5: Retrieved solvent at the end of Phase (3)

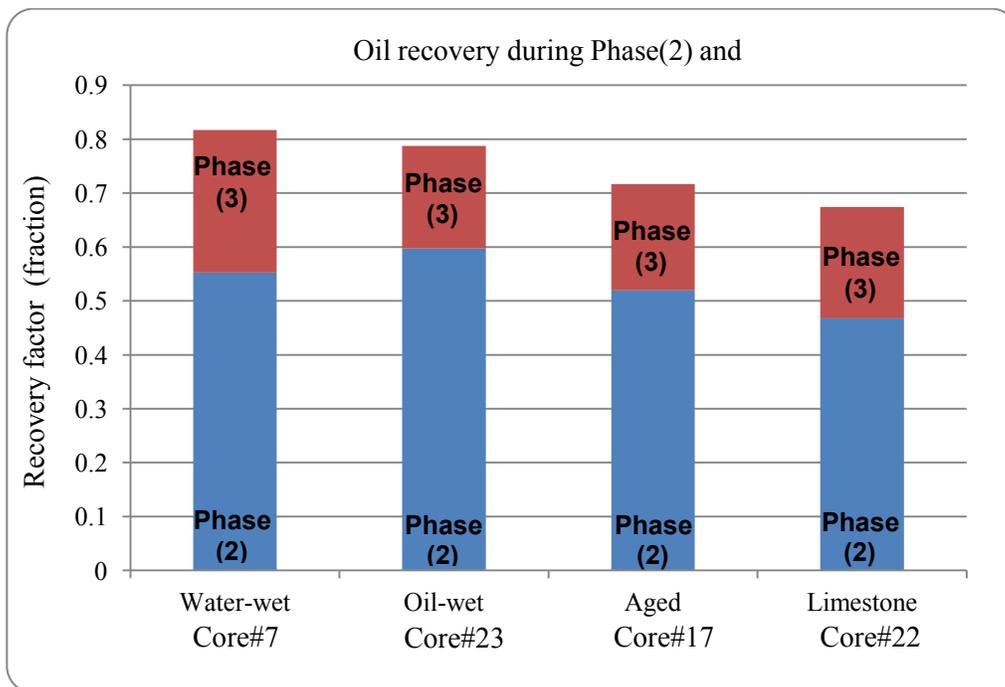


Figure 6: Effect of wettability on oil recovery during Phase (2) and Phase (3) of the process.

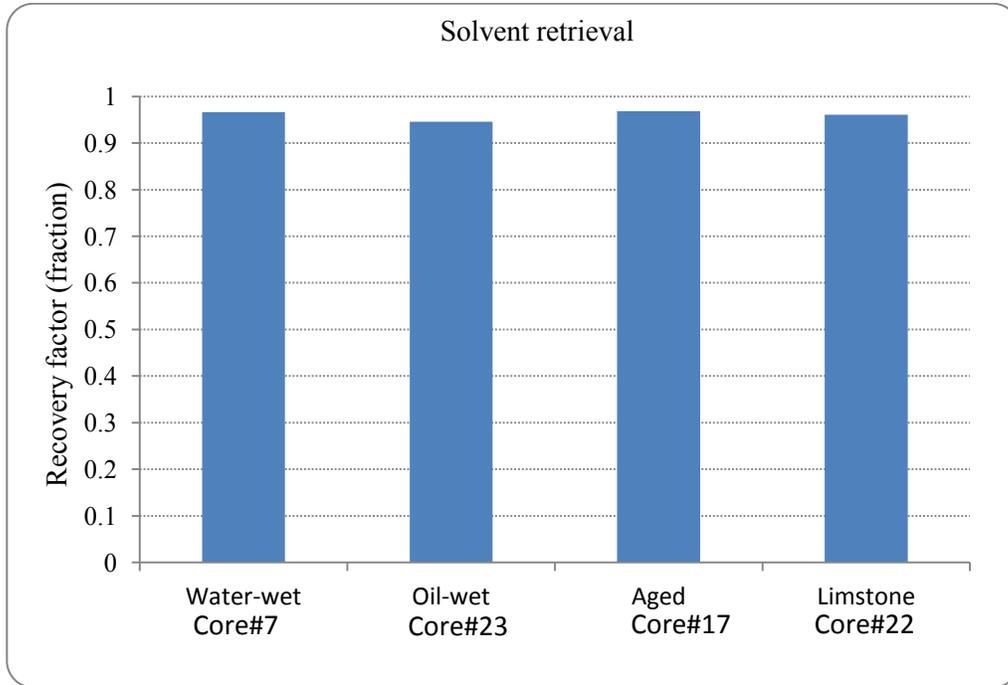


Figure 7: Effect of wettability on solvent retrieval during Phase (3).

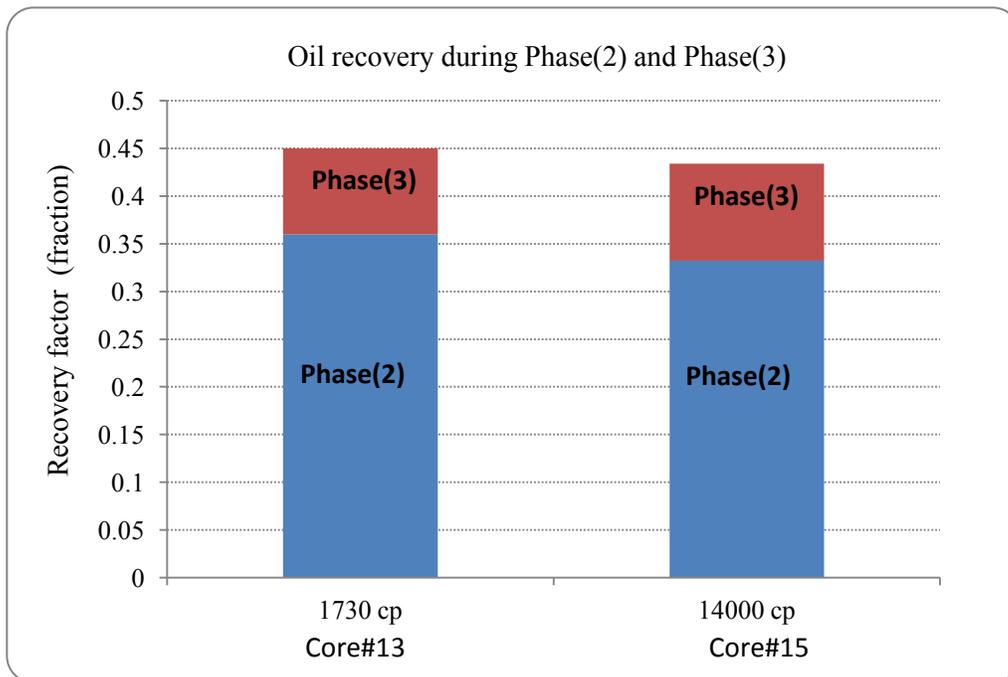


Figure 8: Effect of oil viscosity on oil recovery during Phase (2) and Phase (3).

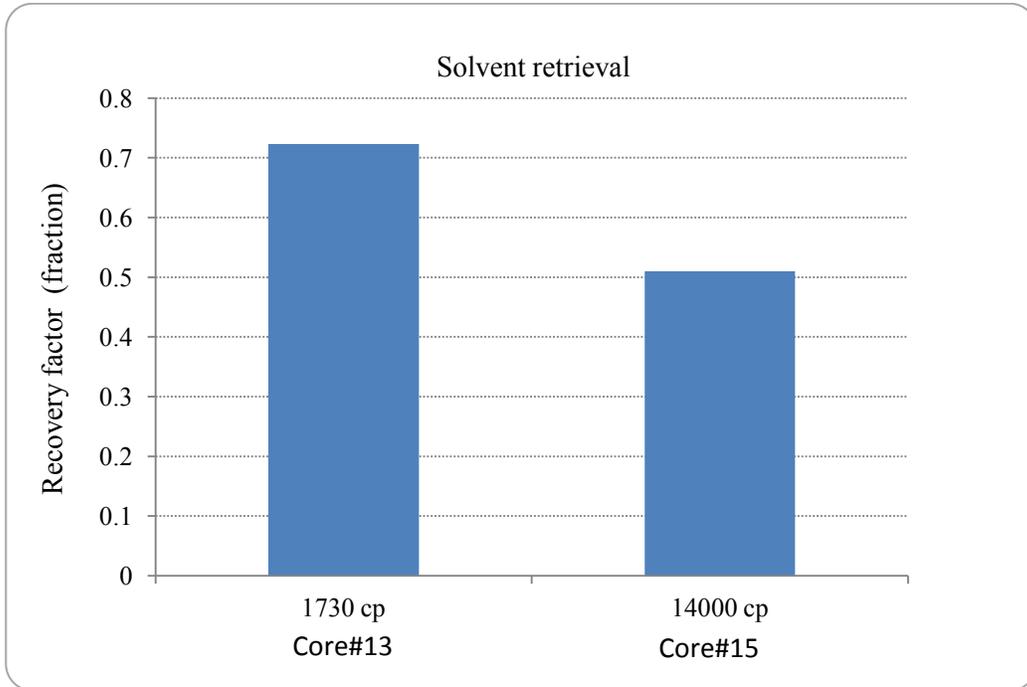


Figure9: Effect of oil viscosity on solvent retrieval.

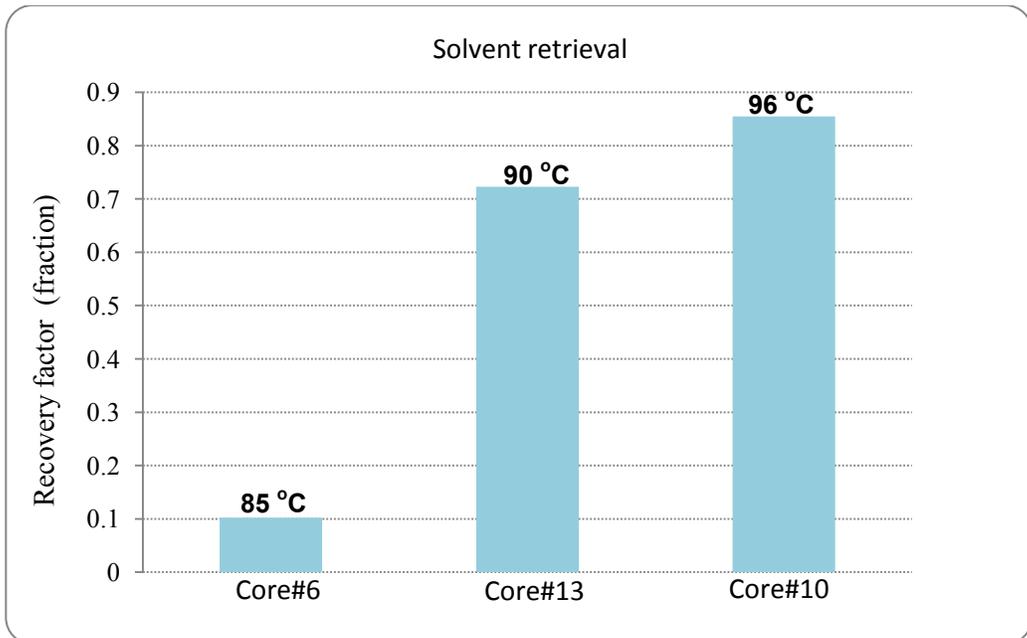


Figure10: Effect of temperature during Phase (3) on solvent retrieval.

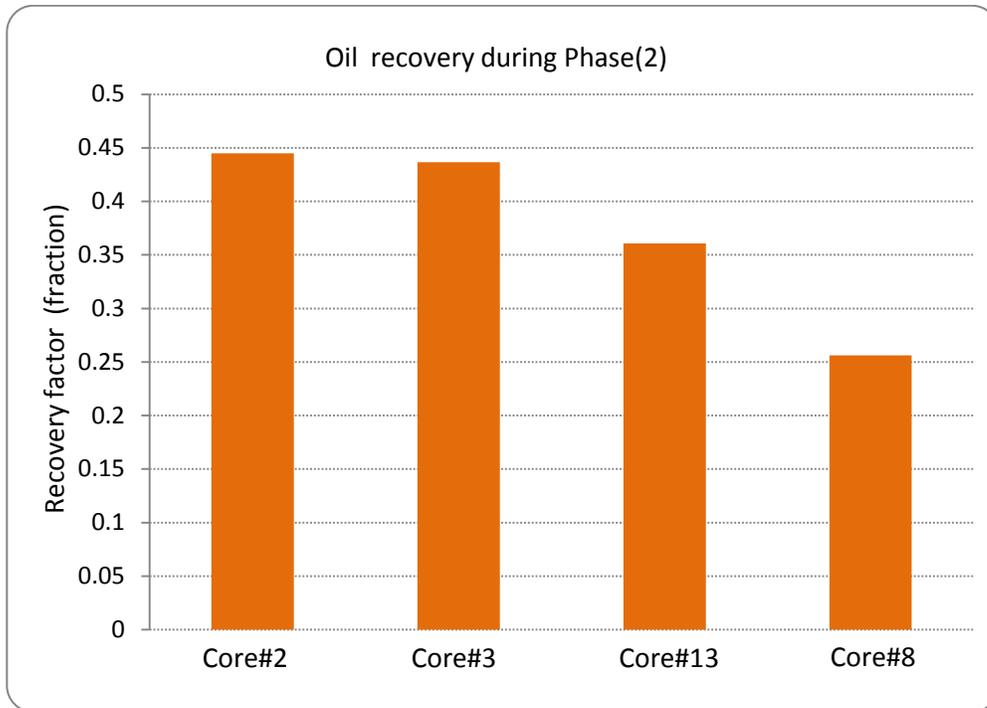


Figure 11: Effect of solvent type on oil recovery during Phase (2).

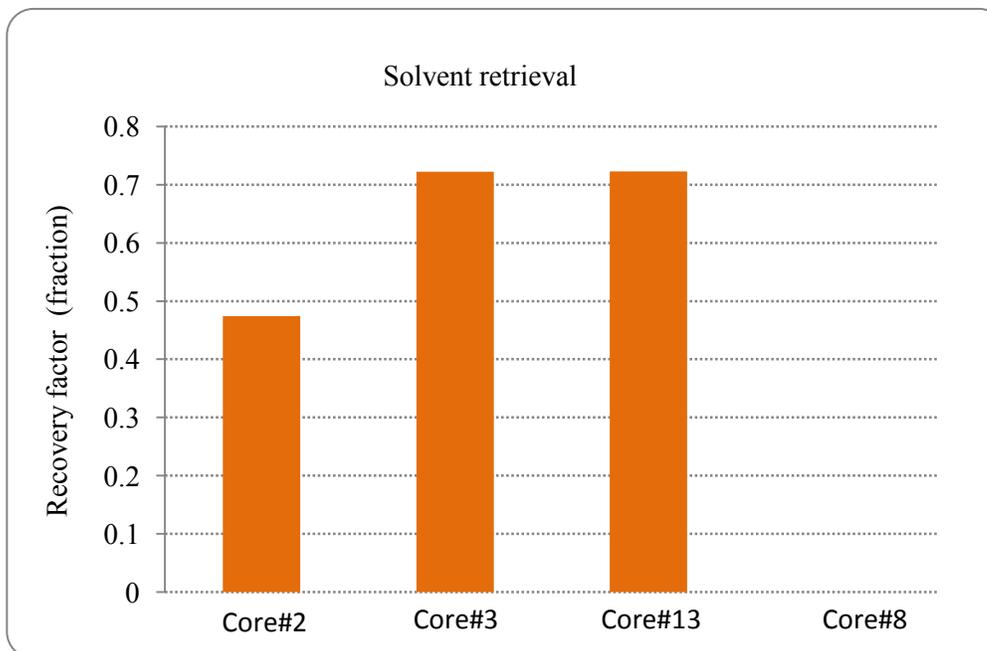


Figure 12: Effect of solvent type on solvent retrieval during Phase (3).

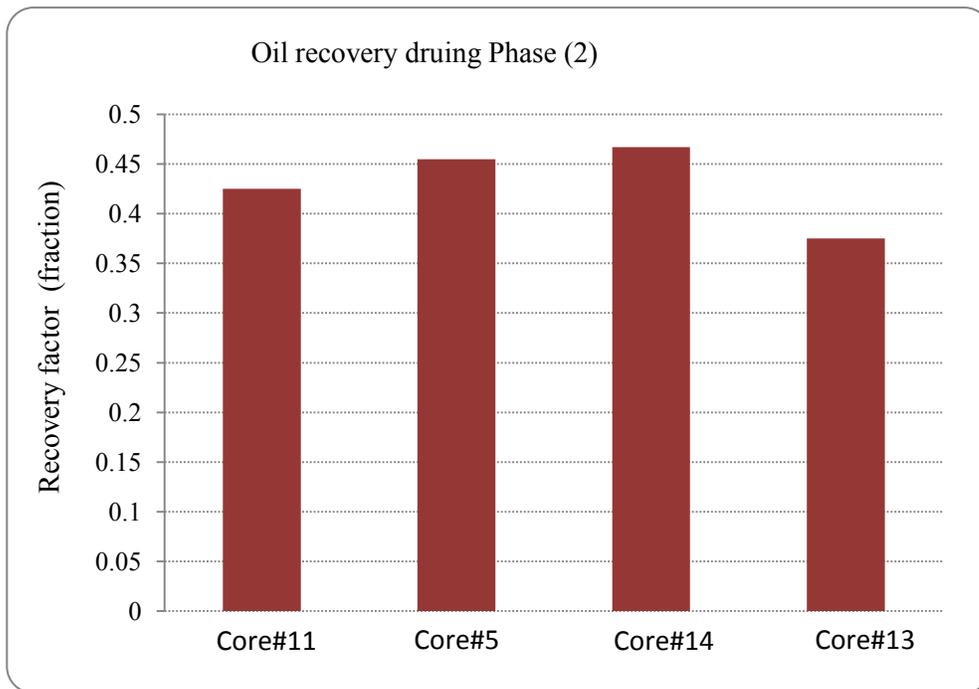


Figure 13: Effect of cycle type on oil recovery during Phase (2).

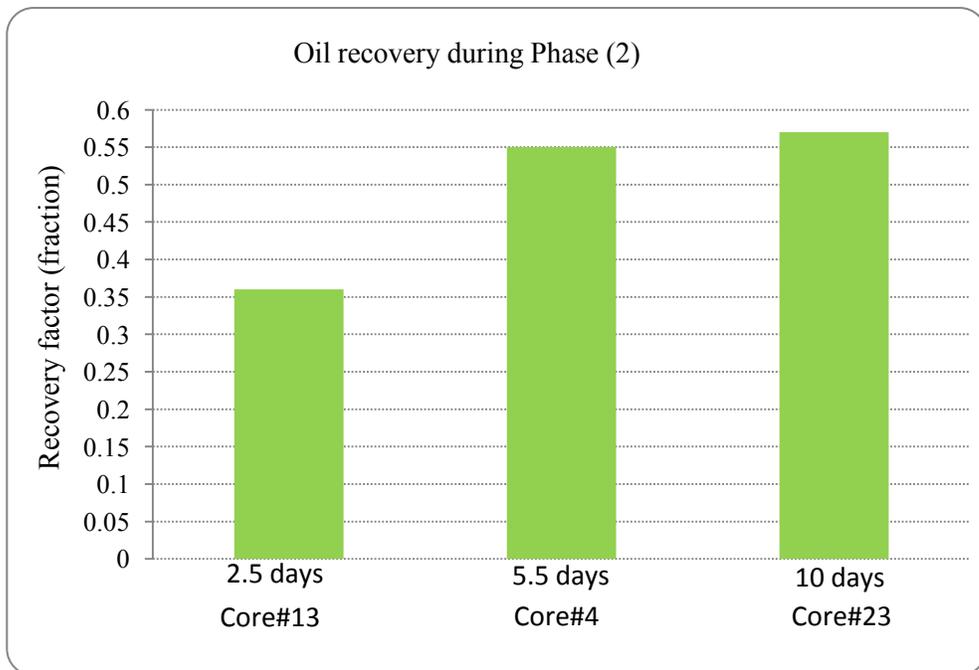


Figure 14—Effect of soaking period on oil recovery during Phase (2), sandstones.

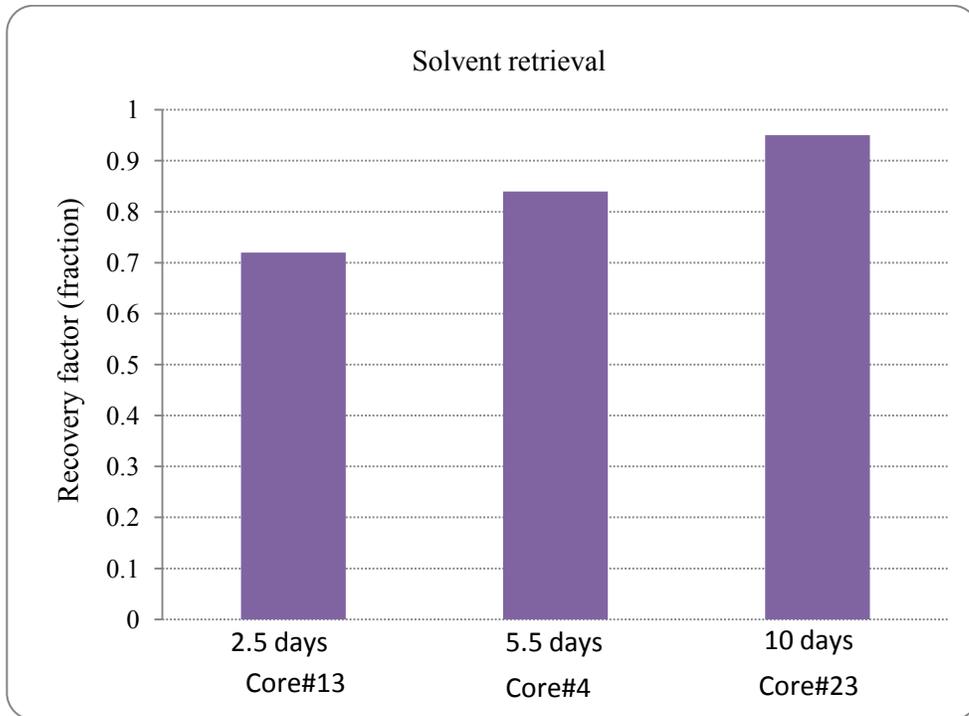


Figure 15: Effect of soaking period on solvent retrieval during Phase (3), sandstones.

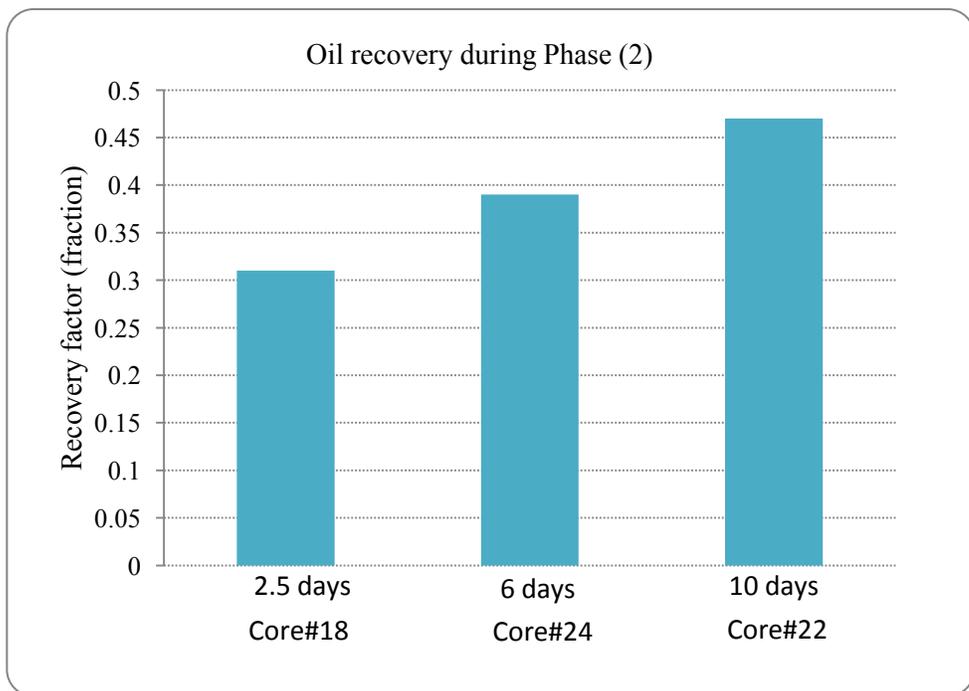


Figure 16: Effect of soaking period on oil recovery during Phase (2), limestone.

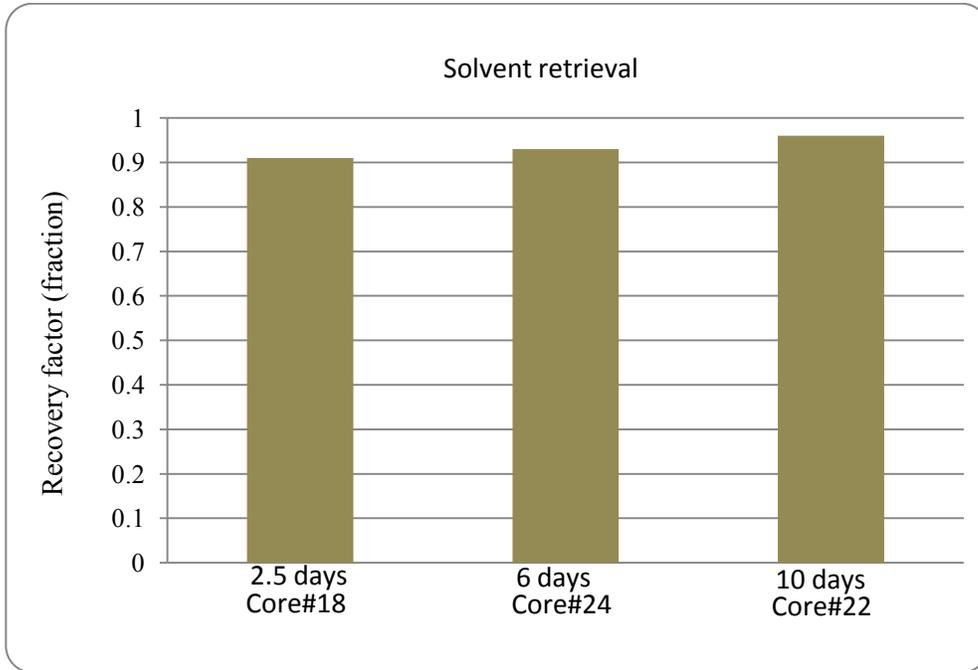


Figure 17: Effect of soaking period on solvent retrieval during Phase (3), limestone.

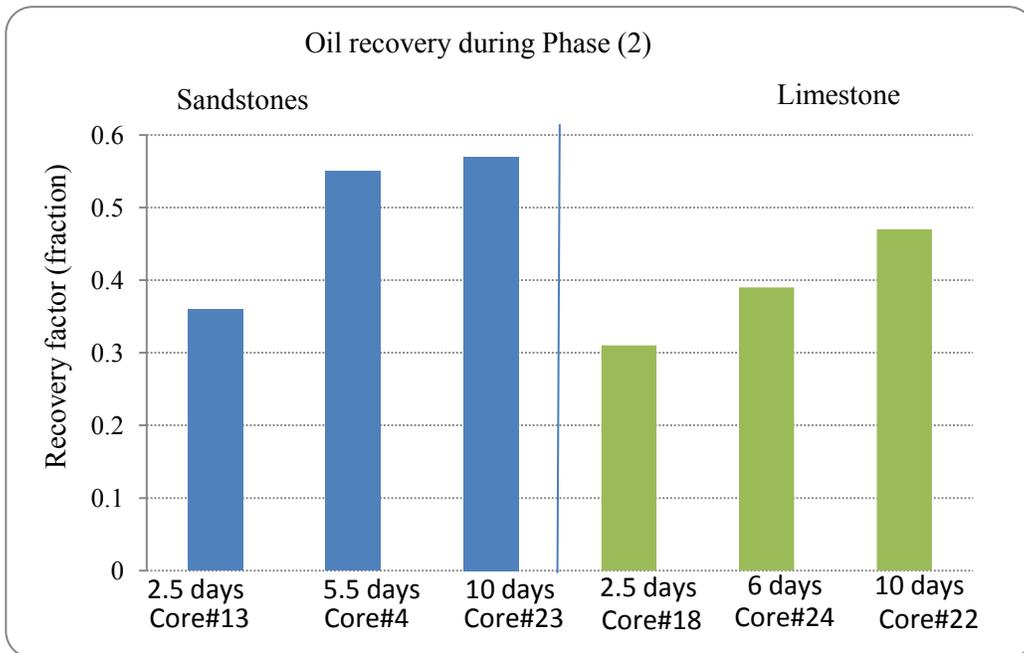


Figure 18: Comparison between oil recovery during Phase (2) for limestone and sandstones at different soaking periods.

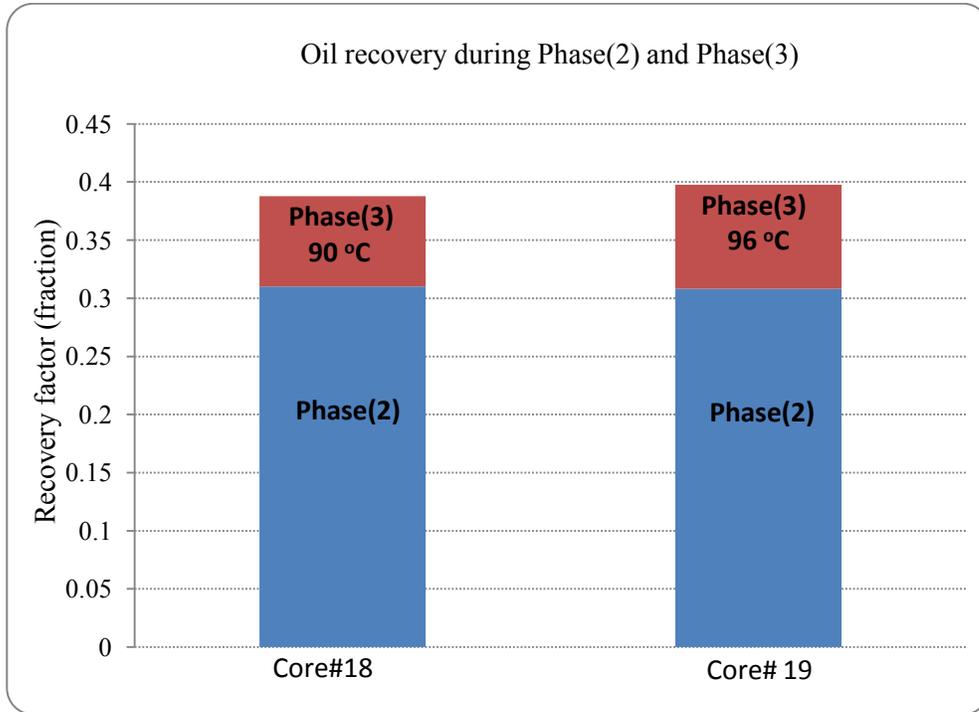


Figure 19: Effect of temperature during Phase (3) on oil recovery.

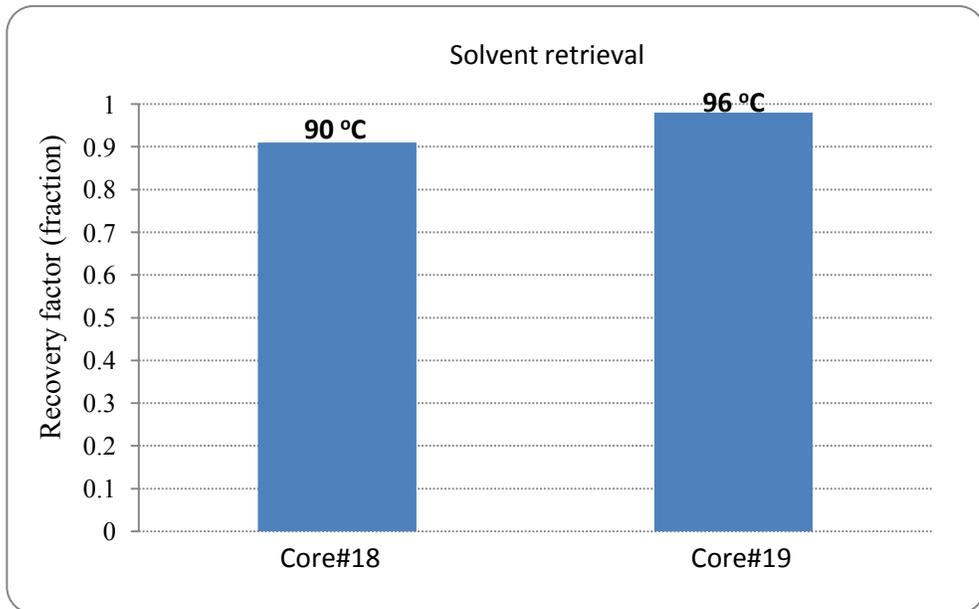


Figure 20: Effect of temperature during Phase (3) on solvent retrieval, limestone.

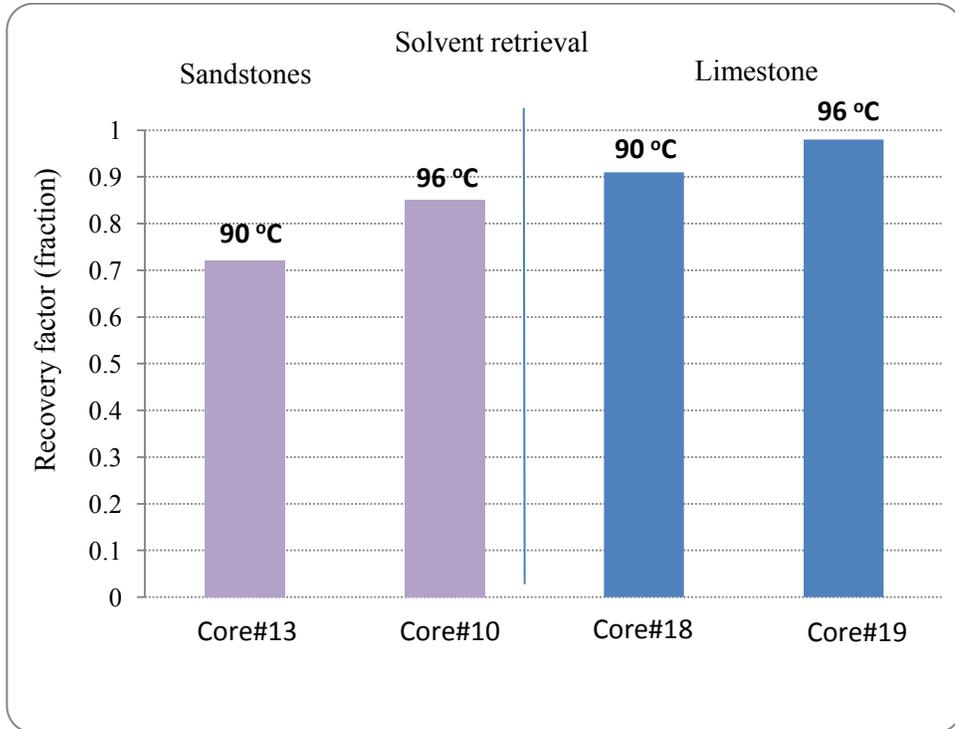


Figure 21: Comparison between solvent retrieval for limestone and sandstones at different temperatures.

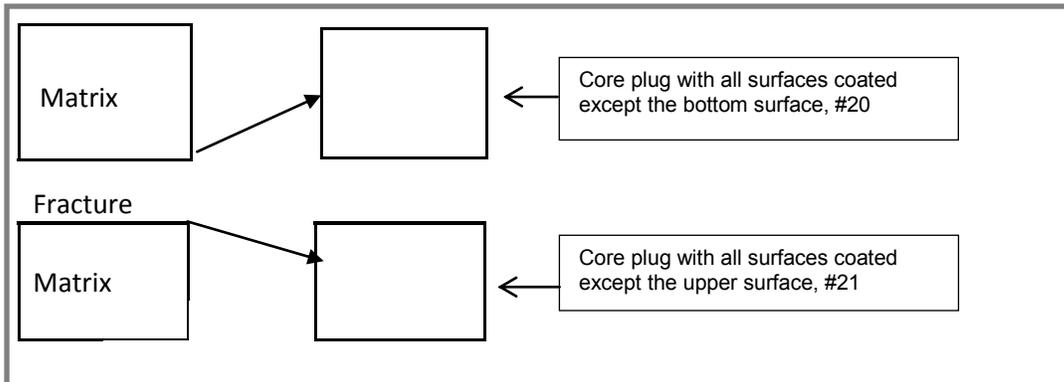


Figure 22: Modeling matrix-fracture interaction and boundary conditions.

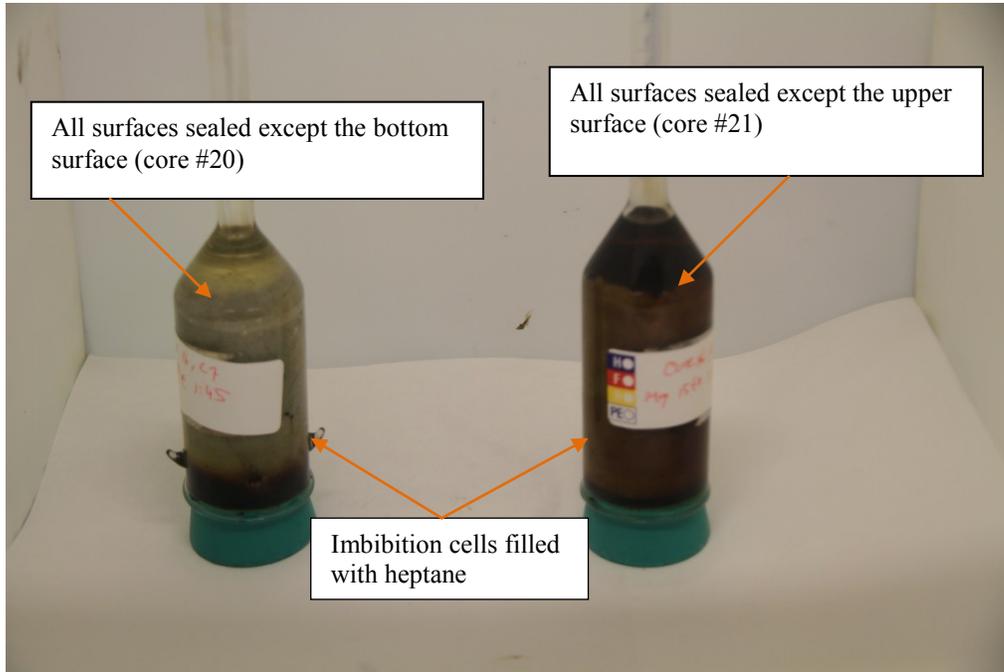


Figure 23: Two imbibition cells contain core samples with different boundary conditions.

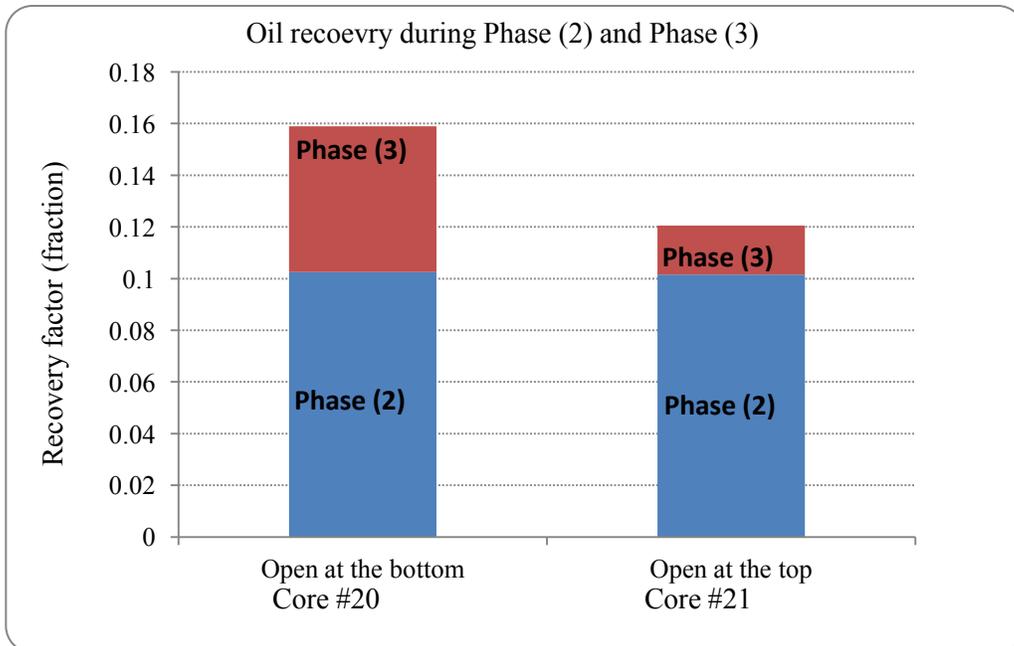


Figure 24: Effect of boundary conditions on oil recovery.

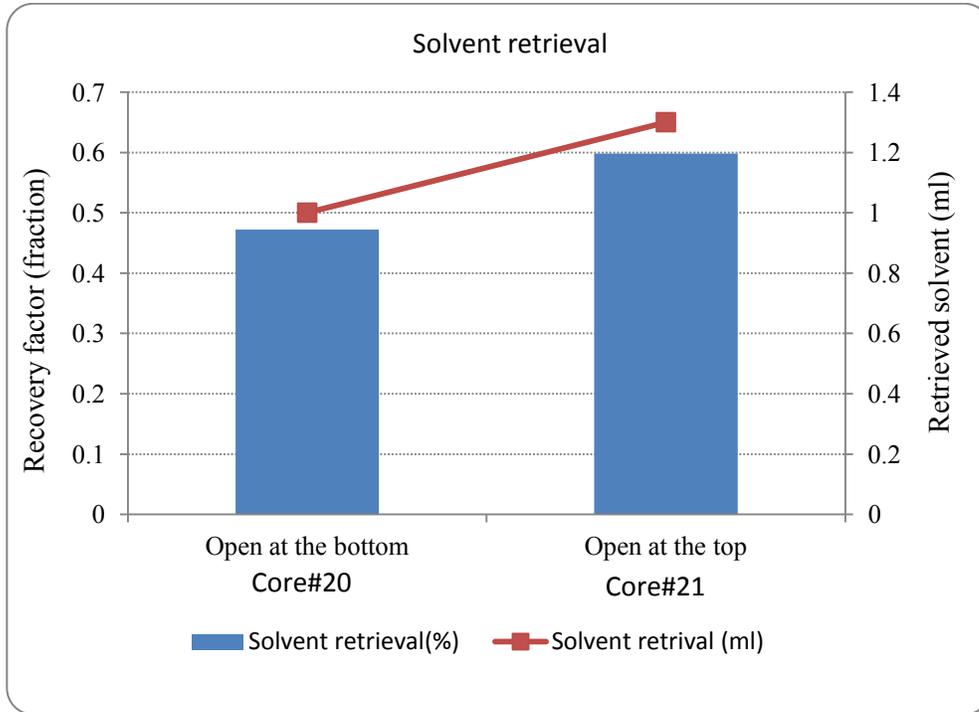


Figure 25: Effect of boundary conditions on solvent retrieval.

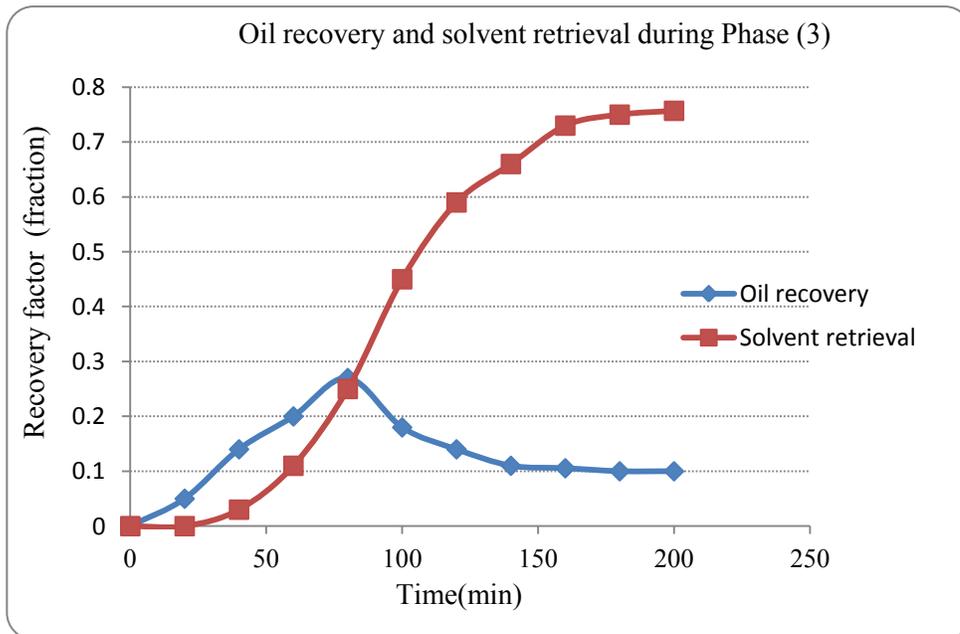


Figure 26: Oil recovery and solvent retrieval during Phase (3) for core # 13.

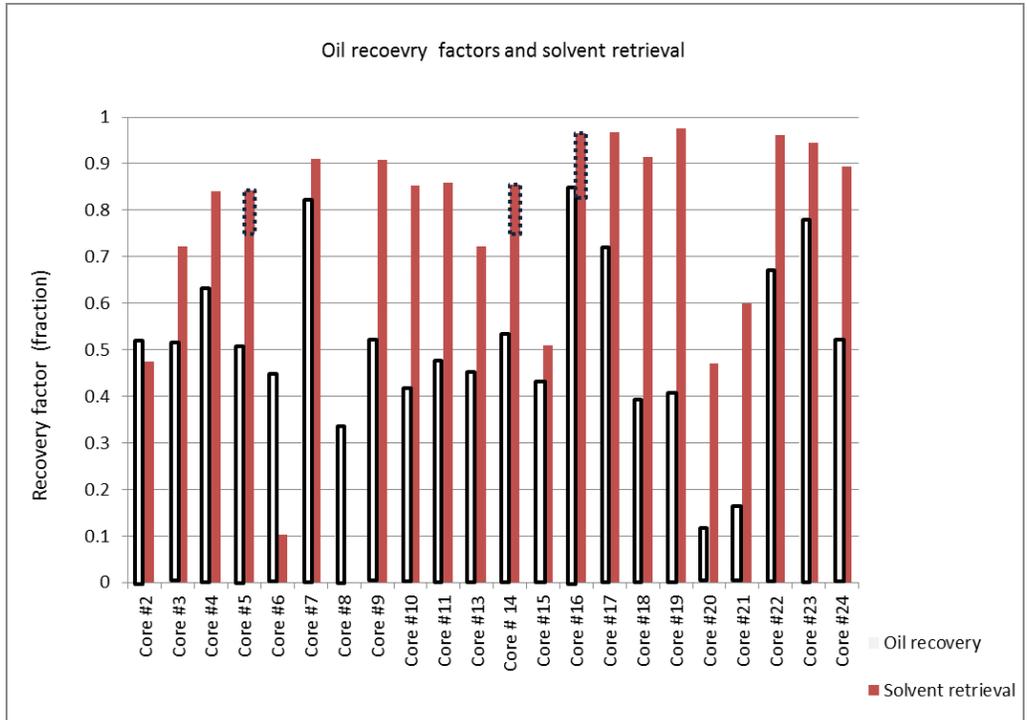


Figure 27: Final oil recovery factor after Phases (2) and (3) and solvent retrieval for the corresponding experiments.

CHAPTER 3: WETTABILITY ALTERATION: A COMPREHENSIVE REVIEW OF MATERIALS/METHODS AND TESTING THE SELECTED ONES ON HEAVY-OIL CONTAINING OIL-WET SYSTEMS

A version of this chapter has been submitted to Advances in Colloid and Interface Science for publication.

Preface

Changing the wetting state of materials is a growing field of research in many areas of engineering and science. In the oil industry, the term wettability alteration usually refers to the process of making the reservoir rock more water-wet. This is of particular importance in naturally hydrophobic carbonates, fractured formations, and heavy-oil systems. This shift in wettability enhances oil recovery in oil-wet and weakly water-wet reservoirs and eventually increases the ultimate oil recovery.

For wettability alteration, two methods have been traditionally used: Thermal and chemical. Although many attempts have been made on reviewing the advancement of research in certain aspects of wettability, a comprehensive review of these techniques, especially in terms of the classification of the chemicals used, has been ignored. In this paper, we begin with this review and provide the past experience of wettability alteration in sandstone and carbonate reservoirs. More than 100 papers were reviewed extensively with an in-depth analysis of different methods suggested in literature. The areas of controversy and contradicted observations are discussed. The limitations and the applicability of each method were analyzed. Concerns on up-scaling laboratory findings to field scale are also addressed. The most promising potential methods are identified and their critical conditions highlighted.

At the end, a selection of reviewed methods is validated experimentally for one of the most challenging cases: Extra heavy-oil and bitumen recovery from fractured-strongly-oil-wet carbonates. Berea sandstone (aged to be oil-wet) and Indiana limestone samples were saturated with heavy oil (3,600 cp). Next, the process was initiated by soaking the cores into solvent (heptane or diluent oil) and the oil recovery was estimated using refractive index measurements. Note that solvent was selected to dilute the oil and recover a considerable amount of oil as any chemical or thermal methods yielded inefficiently low recoveries. After the solvent phase, the samples were exposed to wettability alteration through selected chemicals at different temperature conditions through spontaneous imbibition tests to recover more oil and retrieve the solvent diffuse into the sample back. The most promising wettability alteration agents for each type of rock were marked and optimal application conditions (temperatures, injection sequence) were identified. Selected wettability alteration chemicals were finally tested on the bitumen (5-9 °API-1,600,000cp) containing Grosmont carbonate sample from Alberta, Canada.

It is hoped that this review fills in the gap in the area of wettability alteration processes by summarizing, critically analyzing, and testing the methods suggested in the literature.

1. Why wettability alteration?

Wettability of surfaces is preferred to be hydrophilic or hydrophobic depending on the type of the application. Self-cleaning surfaces, for example, are designed to be hydrophobic. This can be achieved using different techniques such increasing the roughness of these surfaces (Solga et al., 2007). Another mythology to modify surfaces wettability is coating surfaces with low surface energy materials that can be used to render these surfaces super-hydrophobic (Feng et al., 2006). In petroleum reservoirs, the term wettability alteration usually refers to the process of restoring the original reservoir wettability, which is presumed to be water-wet. The target of this restoration treatment is the unrecoverable oil by conventional waterflooding. An early study showed that altering the wettability towards more water-wet increases enhanced oil recovery (Wanger and Leach, 1959). In gas condensate reservoirs, wettability alteration induces a shift in relative gas permeability, which can increase gas well deliverability (Li and Firoozabadi, 2000).

The great role of reservoir wettability on primary oil recovery methods such as water drive was recognized by early research (Bobek et al., 1958). Secondary recovery by waterflooding is directly related to wettability of oil reservoir as well. Wanger and Leach (1959), for example, stated that oil recovery during water flooding for an oil-wet reservoir can be less by 15% in compare with water-wet reservoir. Most of reservoirs, on the other hand, exhibit some degree of oil-wetness and it is rare to find a strongly water-wet reservoir. If reservoir has similar affinity to oil and water, the wettability is defined as neutral, and when some parts of the reservoir exhibits a different wettability than other parts, the term mixed-wet is used (Salathiel, 1973).

Jadhunandan and Morrow (1991) tested the effect of wettability on oil recovery during water injection and concluded that ultimate oil recovery reaches its maximum near the neutral-wet state and not at a strongly water-wet state. Salathiel (1973) showed that reservoirs with mixed wettability can display a higher oil recovery during water flooding than water-wet reservoir. He referred to a field scale experience where a mixed-wet reservoir had an exceptionally high oil recovery compared to water-wet reservoirs. Although there is a general agreement that wettability alteration of strongly oil-wet reservoir is favorable, no conclusive statements can be made about the extent of the alteration that would lead the optimum oil recovery. Consider a porous medium wettability that is altering from strongly oil-wet state to neutral-wet state and then to strongly water-wet state. This shift in wettability may enhance oil recovery by different mechanisms:

1. While the wettability of reservoir is shifting from strongly oil-wet to neutral wet state, capillary forces that retain oil in porous medium is reduced and then eliminated. The

gravitational forces may start playing a role on recovery at this stage. In this range, water contact angle decreases but does not drop below 90°.

2. Alteration of wettability from neutral-wet state toward strongly water-wet state induces capillary imbibition. Both gravity and capillary forces are expected to contribute in oil recovery in this range. Water contact angle need to be brought below 90°.

2. The mechanisms of wettability alteration by Enhanced Oil Recovery (EOR)

As previously explained, a reservoir responds differently to water flooding based on its wettability. The recovery rate becomes lower as the rock behaves more oil-wet. Many of the succeeding enhanced oil recovery (EOR) applications target improving oil recovery by altering the wettability to more water-wet. Several chemical and thermal EOR process were reported to alter the wettability of a reservoir toward water-wetness. The degree of water-wetness that can achieve by EOR immensely depends on how it affects crude oil/brine/rock properties. On the other hand, the mechanisms of crude oil interaction with rock and brine for each petroleum reservoir is different depending on crude oil and brine composition, rock mineralogy, and other reservoir properties. Changing the wetting state of the reservoir requires the understanding of the mechanisms that have altered the reservoir rock surfaces to be oil-wet.

EOR process may change the crude oil/brine/rock properties by two mechanisms: Coating and cleaning (Giraldo et al., 2013). Coating refers to the process of covering the oil-wet layer by water-wet materials. For example, zirconium nanoparticles are hydrophilic and when they adsorb on the rock surface and form nanotexture coating the oil-wet surfaces (Karimi et al. 2012a), wettability changes to more water-wet. Cleaning mechanism is normally associated with surfactant induced wettability alteration. Cationic surfactants, for instance, desorb the oil-wet layer and thus render the surface to a more water-wet state (Standnes and Austad, 2000).

Another example for the cleaning mechanism is oil-wet fines detachment when high temperature is applied (Schembre et al., 2006). When more than one EOR process is applied, both cleaning and coating mechanisms may take place. Giraldo et al. (2013) observed both mechanisms became effective when a dispersion of alumina nanoparticles in anionic surfactants was used to alter the wettability of oil-wet sandstone.

Selection of the EOR process that alters the wettability of reservoir is often related to rock type. For example, cationic surfactants are normally associated with wettability alteration in carbonates

while anionic surfactants were more frequently used for sandstones. Despite the need for wettability alteration in all types of reservoirs, wettability alteration is of greater importance in naturally fractured carbonate reservoirs (NFCRs). This has been reiterated in a large number of publications in this field over more than several decades (Wanger and Leach, 1959; Leach et al., 1962; Salathiel, 1973; Austad et al., 1997; Rao, 1999; Standnes and Austad, 2000; Hirasaki and Zhang, 2004; Golabi et al., 2009; Gupta and Mohanty, 2011; Nasralla and Nasr-El-Din, 2014). In the present paper, 35% of the studies reviewed focused on the wettability alteration in NFCRs. This can be explained by two main reasons. Firstly, most of the NFCRs are either oil-wet or have a neutral wettability. Thus, primary and secondary processes usually fail to mobilize oil that locked tightly by capillarity. Secondly, the NFCRs are composed of matrix and fracture system where most of the oil is contained in the low permeability matrix. This implies that imbibition process is the most reliable mechanism to reach oil that retained in the matrix as viscous forces usually are inefficient to sweep matrix oil in such heterogeneous systems.

In this study, wettability alteration in both sandstones and carbonates was reviewed. Section 3 provides an insight into different mechanism of crude oil/rock/brine interaction. Understanding how a reservoir becomes oil-wet is the first step in restoring the wettability of that reservoir. Section 4 gives a summary of different wettability alteration techniques and the advantages and drawbacks of each tool. The knowledge of how principal forces interact during wettability alteration project is crucial for the success of project design and implementation. Therefore, the interplay among these forces, i.e., gravity, capillary, and viscous forces, are discussed in Section 5. Section 6 covers chemical wettability alteration methods including surfactants, low and high pH solutions, low salinity water and smart water, and nanofluids. Wettability alteration by thermal methods is discussed in Section 7. In Section 8, challenges and opportunities of wettability alteration are summarized. Section 9 provides an overview of new chemicals that may represent potential opportunities as wettability modifiers including ionic liquids and microbial enhanced oil recovery. In Section 10, we report wettability alteration test results in which the selected chemicals from this literature review were used on heavy oil containing sandstone and carbonate samples. Finally, conclusions and recommendations are presented in Section 11.

3. Interaction of crude oil/brine/rock in petroleum reservoir

It is generally agreed that petroleum reservoirs were occupied by water before oil migration at later stages. When oil invaded the porous medium, it did not displace water completely due to the water-wetness of the most of minerals that form reservoir rock such as silica and carbonate (Ehrlich and Wygal, 1977; Abdallah et al., 1986). Consequently, a thin layer of water has remained covering the rock surface. The water layer acts as a barrier between rock surfaces and

oil. If this water layer is preserved through the history of a reservoir, water-wetness of that reservoir will be maintained. The wettability of the reservoir changes when water layer is destabilized as a result of oil/water/rock interaction. As a result of this interaction, the reservoir may become oil-wet (Buckley et al., 1989). Wettability alteration of a reservoir is, therefore, refers to the reversal process by which the reservoir wettability is restored back to be water-wet. Accordingly, understanding the mechanisms by which a reservoir has acquired oil-wet state is the first step in any wettability alteration scheme.

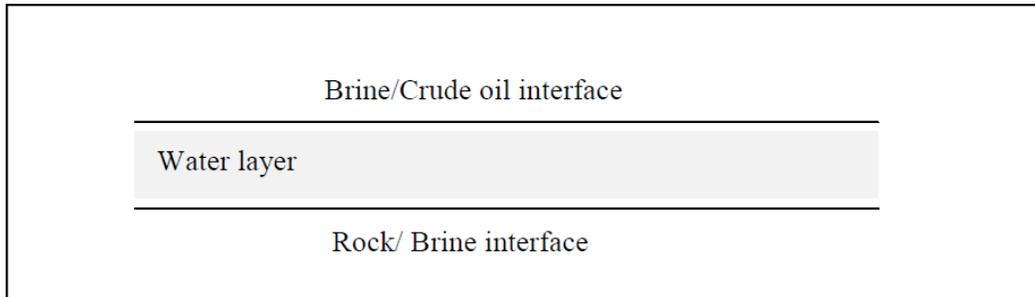


Figure1: Interaction of crude oil/rock brine interfaces.

Destabilization of the layer of water that covers the rock surface (**Figure 1**) occurs when attraction forces between rock/brine and brine/oil interfaces exceed the repulsion forces, water layer will then collapse and oil contacts the rock surface (Buckley et al., 1989). Heavier end of the crude oil contains components that can be adsorbed on the rock surfaces and revert its wettability from water-wet to oil-wet (Bobek et al., 1958; Wanger and Leach, 1959). The type of crude oil components that adsorbs on the rock surface depends on the rock mineralogy. It is believed that basic components in crude oil are adsorbed on silica surface, which is negatively charged on pH ranges under reservoir conditions. Acid components in crude oil such as naphthenic acid (Anderson, 1986; Morrow, 1975) or carboxylic acids (Standnes and Austad, 2000), on other hand, are adsorbed on carbonate surface, which is positively charge (Anderson, 1986; Buckley et al., 1989).

Depending on crude oil/brine/rock interaction, a reservoir may have a homogenous wettability, which can be oil-wet, neutral-wet or wet-wet. The wettability can also be any value in the range of wettability between strongly oil-wet to strongly water-wet (Anderson, 1986). Wettability of a reservoir may not be necessarily homogenous. Salathiel (1973) found that reservoir may exhibit mixed-wet state where different parts of the reservoir have different sates of wettability. The percentage of the oil-wet reservoir in the world is controversial, however, it is generally agreed that most of sandstone reservoirs are water-wet while carbonate reservoirs are believed to be mostly oil-wet (Chilingar and Yen, 1983). Most of oil-wet sandstone reservoirs were found to have considerable clay content.

3.1- Carbonates. An early study by Denekas et al. (1959) examined the effect of surfactant in crude oil on the wettability of limestone. They found that limestone was sensitive to basic nitrogenous surfactants in crude oil. Austad and Standnes (2003) related the oil-wetting state of carbonates to another parameter: acid number (AN). Acid number measures the content of carboxylic acid groups in crude oil (crude oils with higher acidic number are more likely to render the carbonate surface oil-wet). They found no direct effect of asphaltene content of crude oil on the wettability of carbonate. A study presented by Zhang and Austad (2005) reached a similar conclusion on the effect of AN on wettability of carbonate. Carbonate rock sample were aged in crude oils that had AN range of (0.17-2.07 mg KOH/g). Samples exhibited different wetting states based on AN. Crude oils with higher AN were more able to change the wettability of samples to be oil-wet. Xie et al. (2010) showed the same effect of AN on volcanic reservoir plugs.

3.2- Sandstone. Acid number may not be as an important factor in sandstones as in carbonates. This is attributed mainly to the negative charges of sandstone, which favors basics over acids (Anderson, 1986). Buckley et al. (1998) saturated sandstone with eight types of oils with different acid/base number values. No correlation between the wettability index and acid number was found. Denekas et al. (1959) conducted an experimental study on the wettability modification by crude oil in sandstone. A distillation process of crude oil was performed and fractions with different molecular weight (MW) were collected and used to saturate sandstone core samples. The wettability of the core samples was then measured by spontaneous imbibition test. Fractions with low MW were not able to change the wettability of sandstone. As MW of fractions increased, sandstone became more oil-wet. The maximum degree of oil-wetness was achieved with the heavier components that remained after distillation. This study concluded that surface active materials that change the wettability of sandstone possess a high MW and that when sandstone is saturated with higher concentrations of these materials, a more oil-wet state will be acquired. Buckley and Liu (1998) suggested four mechanisms of wettability alteration by crude oil including polar interaction, surface precipitation, acid/base interaction, and ion binding. Crude oils with high base number and low acid number can alter the wetting of silicate surfaces by acid/base interactions. Crude oils with higher AN and low base number (BN) can alter wetting by ion-binding interactions. Crude oil that contains asphaltenes alters the wettability by surface precipitation. A correlation between AN/BN, API degree, and wettability index showed that API degree is the governing factor in wettability alteration by crude oil for sandstones.

Another possible mechanism of wettability alteration by crude oil in sandstone is the effect of clay content. Schembre et al. (2006) observed that sandstone became more oil-wet when the clay content increased. They referred to a previous study by Tang and Morrow (1999) which found that clay was a dominant factor in changing the wettability of Berea sandstone to toward water-

wetness. Vledder et al. (2010) explained that at high concentration of multi divalent ions in high salinity reservoir brine minimizes the negative electrical charge on clay surface resulting a reduction in repulsive force. Surface active material in crude oil will then adsorb on clay surface rendering it oil-wet.

A conclusion that can be drawn from this discussion is that AN is the most important factor of changing wettability of carbonates by crude oil; water-wetness increases as the AN decreases. In sandstones, API, asphaltene content, and clay content are the most dominant factors that control the wettability alteration by crude oil. Integration of API, AN, clay content, and asphaltene content measurement would provide valuable information to evaluate the mechanism or composite of mechanisms by which the original wettability of sandstone and limestone is changed to be oil-wet.

4. Wettability alteration measurements

Reliable wettability alteration measurement tools are essentially needed to evaluate and monitor the efficiency of wettability alteration treatment. It can be observed that most of the above reviewed studies focused on spontaneous imbibition tests to evaluate the wettability of core samples. Other options exist to measure wettability before and after wettability treatment. Anderson (1986) provided a review of different types of wettability measurement tools. Each of these tools measures the manifestation of wettability alteration from different perspectives. There is no agreement, however, on standard wettability alteration test (Rao, 1999). The following is a summary of common wettability measurement tests.

4.1- Contact angle. Contact angle can be defined as the point at which oil and water interface meet at rock surface. It can be used to analyze the alteration of surface wettability as it measures the shift in rock surface affinity of one fluid to another in a continuous manner. In other words, the contact angle can be measured both in static and dynamic states (Morrow, 1990). Many studies on wettability alteration processes were carried out using contact angle measurement; however, there is no universal protocol on how this test should be performed. Techniques of contact angle can be as simple as taking readings of contact angle using photos by digital camera or as complicated as taking high resolution images using environmental scanning electron microscope (ESEM) (Wei et al., 2003). Yuan and Lee (2013) provided a comprehensive review on the recent advancements on contact angle measurement techniques.

The question of how to define wettability by contact angle values and terminology use to describe the level of wettability are still controversial. However, it is generally accepted to use water

contact value greater than 90° to indicate oil-wet state and water contact angle less than 90° to describe water-wet state. The neutral state is determined by a contact angle that is about 90° . Two types of dynamic contact angle are usually measured: advance contact angle and receding contact angle. Advanced contact angle is more frequently utilized to assess the wettability alteration. Morrow (1975) provided relationships between intrinsic contact angle and advanced/receding contact angles under different roughness conditions.

Reduction in water contact angle on a rock surface implies that wettability of that surface has changed to more water-wet and less oil-wet. Solid surfaces usually made oil-wet by aging in crude oil or coating them with chemicals such as CTAB (Zhang et al., 2006) or SURFASILTM (Al-Bahlani and Babadagli, 2008). To assess the degree of wettability alteration after these processes practically, static or dynamic contact angle measurements can be applied. Contact angle measurements can also be performed at high temperatures. Rao (1999) was able to measure receding contact angle on quartz surface at a temperature range from 25 to 200°C .

Although contact angle allows fast and economical mean of wettability alteration assessment, it has many limitations. It is, for example, highly sensitive for contaminations. Accurate measurement of wettability alteration by contact angle at surfaces that exhibit high contact angle hysteresis represents another challenge. There is no agreement in literature on whether it is more representative to measure contact angle on mineral plates or porous rock plates. Mica and silica (typically glass) are used to represent sandstones while marble and calcite are used in place of carbonate. While using porous rocks may be more realistic, issues such as surface heterogeneity may interfere with the accuracy of the measurement. On the other hand, measuring contact angle on pure mineral may be misleading as the mineralogy of the rock will not be accurately represented. Thus, another challenge emerges: finding a representative surface that can capture the properties of the surface of the reservoir rock properly (Morrow, 1975). Many studies showed that composition and mineralogy can have a great effect on wettability. Sharma et al. (2011) stated that contact angle cannot conclusively affirm the ability of surfactant to change the wettability. They experimentally demonstrated that some of the surfactants that were able to change the wettability on calcite plates failed to imbibe spontaneously into reservoir core sample. A common practice in contact angle measurement that is used to reduce the limitation of this technique is repeating a measurement several times until the minimum acceptable margin of error is achieved.

Mohammed and Babadagli (2014b) found that ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate BMIM BF₄ is able to imbibe spontaneously into oil-wet limestone but they did not test it on sandstones. Contact angle measurement serves as a faster (and economical) tool to explore if this ionic liquid affects the wettability of sandstone. **Figure 2** shows droplets of oil on

oil-wet glass surface that immersed in BMIM BF₄ solutions at different concentrations. As seen, the contact angle is reduced as concentration increased from 0.25 wt.% to 0.5 wt.% and then to 1.0 wt. % indicating wettability alteration of silica surface from oil-wet to water-wet. Imbibition tests on sandstone can be used to confirm this observation.

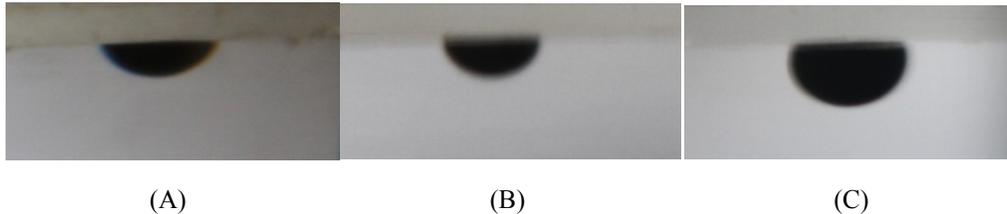


Figure 2: Contact angle images of oil droplets on oil-wet glass surface that immersed in A: 0.25 wt. % ionic liquid solution, B: 0.5 wt. % ionic liquid solution, and C: 1.0 wt. % ionic liquid solution.

4.2- Spontaneous imbibition (SI). SI test measures the ability of the wetting phase to displace the non-wetting phase under static conditions. The relationship between capillary pressure and wetting phase saturation is highly dependent on the wettability of the rock surfaces. Water easily displaces oil in water-wet system as it has positive capillary pressure. In oil-wet systems, capillary pressure is negative and water does not imbibe into porous medium as oil is firmly attached to the rock surface by capillarity.

The SI test demonstrates the contribution of capillary and gravity forces during wettability alteration and can be conducted in the lab by placing a core sample that saturated with crude oil in a graduated cell filled with water. Imbibition curve can then be established by plotting oil production versus time. Imbibition curve is used to interpret the wetting properties of core samples. As will be explained later, other visual information can be obtained from imbibition tests such as the contribution of each face of the core in the oil recovery, as a delineation of wettability. The production of oil from lateral surfaces of the core indicated that counter-current capillary imbibition took place. The SI test may also be used to study the effect of boundary condition on the imbibition process. Due to all of this valuable information that can be generated by the SI test; it is considered one of the most reliable measurements of wettability alteration.

Figure 3 shows the spontaneous imbibition curves for two limestone core samples from the same core sample (Mohammed and Babadagli, 2014b). One core was soaked into distilled water while the other one was immersed into cationic surfactant C12TAB solution at 1.0 wt.%. A quick look to this curve indicates the oil-wet nature of the core samples as no water imbibes into porous medium

spontaneously. The gravity forces barely displace 2% PV as it is resisted by negative capillary forces. Spontaneous imbibition curve of the surfactant solution shows a different behavior. After about 10 days, C12TAB solution starts imbining into the core slowly. The rate of spontaneous imbibition increases with time showing the alteration of core wettability. When core wettability is adjusted to less oil-wet state, capillarity no longer retains the oil and gravity forces take place.

As wettability altered to be water-wet, capillary forces dominate the oil displacement. It is also apparent that there is a cross over region in the imbibing mode from gravity dominated displacement to capillary dominated flow. This behavior is -in a way- contrary to what we see in the spontaneous imbibition of low-IFT solutions in water -wet systems where flow is crossed over from capillary dominated flow at the start to gravity controlled regime at late times.

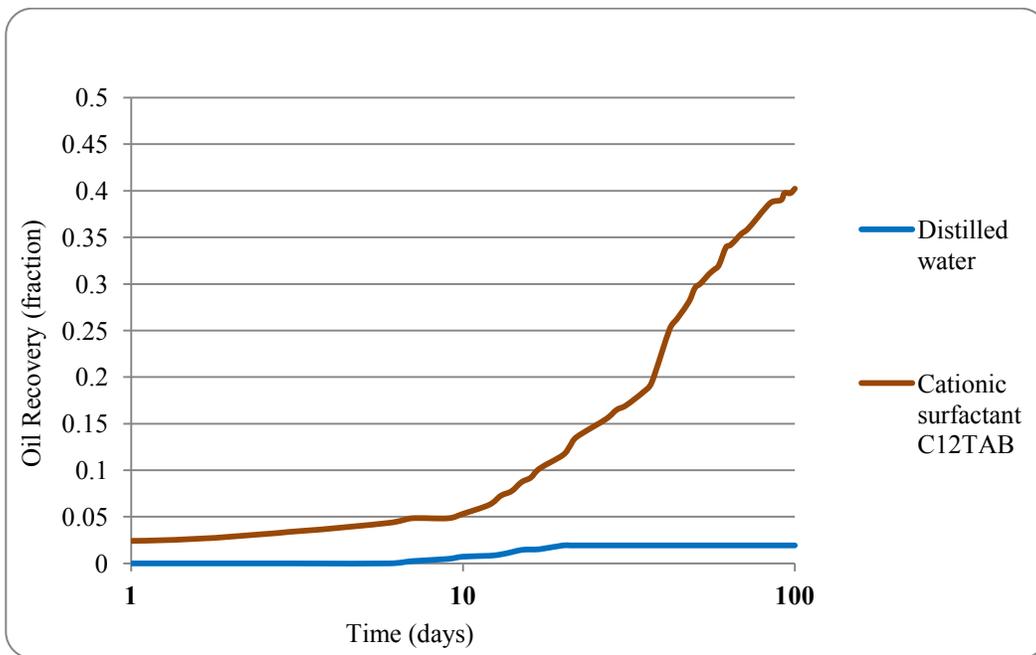


Figure 3: Spontaneous imbibition behaviour for limestone cores (reproduced after Mohammed and Babadagli, 2014b).

Høgnesen et al., 2006 used a special imbibition cell to monitor the oil that is produced from the top surface by gravity forces and that which produced from the lateral surfaces by capillary forces. A chalk core was immersed in C12TAB at 1.0 wt.% concentration. They observed that most of the oil is produced from the top surface from early stages of imbibition. The main difference between the imbibition of low-IFT solutions in water-wet systems and the imbibition of C12TAB in oil-wet carbonate is the dynamic alteration of wettability by C12TAB. The ability of C12TAB to change the wettability of oil-wet toward water-wetness carbonate was explained by Standnes and Austad (2000).

4.3- Surface imaging tests. Surface imaging techniques such as scanning electron microscope (SEM), atomic force microscopy (AFM), and nuclear magnetic resonance (NMR) give insight into changes in rock surface characteristics as a result of wettability modification treatment. Schembre et al. (2006) used SEM images to understand the mechanisms by which sandstone surfaces become water-wet at high temperature. In a study of wettability alteration by nanofluids, Karimi et al. (2012a) used SEM images to investigate the adsorption of zirconium nanoparticles on carbonate surfaces.

4.4- Zeta potential measurement. Zeta potential measurements were applied by many experimental studies to measure the change in electrostatic forces. A shift in Zeta potential on carbonate surface from positive values to negative values was used to explain the mechanism of wettability alteration by alkaline anionic surfactant in carbonate reservoir (Hirasaki and Zhang, 2004).

Wettability alteration is a complex process that involves a change in many surface properties. A review of different methods for wettability alteration measurements shows that each wettability alteration test can give valuable information to evaluate the wettability alteration process. However, comparative study of results obtained by different research studies may not be an easy task as each test measure different surface properties and perform by a different methodology, and therefore they may not be easily accessible methods and are also expensive (SEM, AFM, NMR, Zeta potential).

5. Capillary and gravitational forces as an indicator of the state of wettability

Fluids displacement in porous medium is controlled by three types of forces: capillary forces, gravity forces, and viscous forces. In oil reservoir, the extent and the rate of oil recovery are determined by the interplay of these forces. Two useful numbers that describe the relationship between these forces are the Inverse Bond Number (BN^{-1}) and Capillary Number (CN) as described below:

$$\text{Inverse Bond Number} = \frac{\text{Gravity forces}}{\text{Capillary forces}} \quad \text{Capillary Number} = \frac{\text{Viscous forces}}{\text{Capillary forces}}$$

$$F_{\text{capillary}} = 2\sigma_{\text{ow}} \cos \theta_c / r \quad (1) \quad F_{\text{gravity}} = \Delta\rho gh \quad (2)$$

$F_{\text{capillary}}$: Capillary forces F_{gravity} : gravity forces

σ_{ow} : Oil-water interfacial tension

The dominator in both relationships is capillary force, which is a function of interfacial tension (IFT) between oil and water, radius of pores (r), and surface wettability, which is represented by contact angle (θ). For homogenous water-wet reservoirs, capillary number plays an important factor in recovery evaluation and viscous forces controls the dynamic of fluids displacement. Increasing capillary number by reducing capillary forces is favorable as it reduces the residual oil, which is normally performed by reducing IFT. For heterogeneous oil-wet reservoir and naturally fractured carbonate reservoirs (NFCRs) in particular, the viscous forces cannot be applied efficiently as high pore volume matrix possess low permeability and much lower volume fracture system controls the flow by viscous displacement. Fluids dynamic in this type of reservoir is controlled by the inverse BN.

Imbibition into wetted cylindrical tubes could be scaled depends on the cosine of the contact angle (Morrow Mason, 2001). According to **Eq. 1**, the sign of the capillary forces may be reversed from negative to positive value depending on the wettability of reservoir. In a water-wet cylindrical core sample, contact angle would be less than 90° and capillary forces initiates and maintains imbibition of water and the displacement of oil in counter current fashion. In an oil-wet core, the contact angle is greater than zero, and no capillary imbibition takes place.

Two parameters that can be changed to enhance the capillary forces are oil/water interfacial tension (σ_{ow}) and surface wettability ($\cos \theta_c$). While reduction in water contact angle is favourable for capillary imbibition, interfacial tension should be maintained as high as possible. These two parameters, however, are not independent of each other. This fact complicates the process of wettability alteration as many of wettability modifiers change the wettability to water-wet state but they reduce the interfacial tension at the same time. The Young equation gives the contact angle as a function IFT tensions between oil and rock, oil and water, and water and rock:

$$\cos \theta_c = (\sigma_{os} - \sigma_{ws}) / \sigma_{ow} \quad (3)$$

- σ_{os} : Oil-solid interfacial tension
- σ_{ws} : Water-solid interfacial tension
- σ_{ow} : Oil-water interfacial tension
- θ_c : Contact angle of oil and water in solid surface

Consider a water-wet cylindrical core sample that was saturated with oil placed in an imbibition cell filled with water. Reducing oil-water interfacial tension (σ_{ow}) would:

- a) Directly reduce capillary forces according to Eq. 1 and
- b) Reduce contact angle according to Eq. 3, which increases capillary forces according to Eq. 1.

Reducing θ_c may also be achieved by decreasing ($\sigma_{os} - \sigma_{ws}$) value; i.e. reducing the affinity of rock to oil in favor of water. Reducing oil-water interfacial tension weakens capillarity and oil is expected to be produced by gravitational forces. Many research studied the capillary imbibition process, which is driven primarily by wettability at different BN^{-1} values. At a high BN^{-1} , fluid dynamic is controlled by the large capillary forces (Schechter et al., 1994; Al-Lawati and Saleh, 1996). When the BN^{-1} is low, both capillary and gravity forces contribute to oil recovery. In a study by Schechter et al. (1994), different IFT values were tested. When the IFT was high (38 dyne/cm), counter current imbibition was observed at early times and oil was produced from lateral faces of the core sample. At an intermediate IFT (around 1.07 dyne/cm), oil production was

observed from all faces of the core indicating that both capillary and gravity forces took place. A minor increase in oil recovery was observed in comparison with high IFT. When the IFT was as low as 0.1 dyne/cm, oil recovery was slow but eventually reached a higher recovery than the other two cases. Similar observations were made by (Babadagli et al, 1999) for kerosene-surfactant solution systems.

The flow of fluids at low IFT is controlled by gravity forces compared to oil recovery by imbibition for a range of IFT. Schechter et al. (1991) and later Babadagli (2001) showed that this can be scaled by the gravity scaling group and higher oil recovery is acquired at low IFT. They also observed that the reduction of residual oil entrapment at low IFT enhanced the oil recovery at low IFT when no initial water is present in the system. An explanation to this reduction of residual oil at low IFT was discussed by Al-Lawati and Saleh (1996). They showed that relative permeability of oil and water becomes low in the counter current type of flow that is typically encountered during capillary imbibition, and each fluid resists the flow of the other fluid. During the gravity dominated imbibition, fluid flow is in co-current fashion and relative permeability of both fluids is high. Note that flow is governed by the density difference and the permeability of the core. Although final recovery is higher for low IFT, the rate of imbibition is higher for intermediate IFT (Morrow and Mason, 2001; Schechter et al, 1991). When the IFT value is intermediate, recovery by gravity force is in co-current manner (thus relative permeability is high) and the capillary forces also contribute to the imbibition process (Babadagli, 2001). Al-Lawati and Saleh (1996) referred to an earlier study by Saleh and Graves (1993) in which they suggest that there is critical IFT after which considerable amount of trapped oil can be freed. At that critical IFT, oil bubbles elongate and then broke down into smaller bubbles. The small bubbles then flow through the pore throats easily. In a study by Morrow and Mason (2001) on the effect of IFT on oil recovery by imbibition, the researchers found that reducing IFT may increase or decrease imbibition depend on the contribution of gravity forces. Babadagli (2003) documented a similar observation regarding the rate effect lowering IFT. Morrow and Mason (2001) observed that higher ultimate oil recovery is achieved by the lowest IFT. Babadagli (1999) stated that low IFT surfactant solutions can be used to contact the part of the matrix that can be inaccessible by the brine.

The above discussion shows that reducing IFT gives rise to gravity forces. The magnitude of gravity forces is a function of the density difference between oil and water. In heavy oil, extra heavy oil, and bitumen reservoirs this value is quite low. Høgenesen et al. (2006) stated that the gravity forces will dominate the flow of fluids during wettability alteration by cationic surfactant. In a study of the wettability alteration by thermal treatment in carbonate reservoirs, Al-Hadhrani and Blunt (2001) showed that the gravity forces may only be efficient in recovering oil at the bottom part of reservoir. The hydrostatic head in the upper part may not produce quite enough

gravitational force to displace the oil spontaneously. Therefore, it was concluded that the capillary forces should be essentially activated to increase oil recovery.

The main mechanism of wettability alteration by cationic surfactant is to change wettability to the extent that induces spontaneous imbibition (Standnes and Austad, 2000). Alkaline anionic surfactants, on the other hand, adopted a mechanism that reduces the capillarity forces and oil is mainly recovered by the gravity forces (Hirasaki and Zhang, 2004). The determination of whether wettability alteration by cationic surfactant or alkaline anionic surfactant is more efficient for carbonate reservoir depends on many factors. Understanding which mechanism is more suitable for a reservoir wettability alteration depends on many factors such as crude oil properties including density and viscosity, reservoir characteristic such as permeability, current status of wettability, size of the matrix and contact area between the fracture and matrix, vertical continuity of the reservoir, and the effect of boundary condition.

The contribution of the capillary and gravity forces on incremental oil recovery is very much related to the effect of boundary conditions as well (Babadagli, 1999). Density difference evaluation is also important (Hognsen et al., 2006). For the heavy oil and bitumen cases where the density of water and oil is almost identical, gravity contribution should not be overestimated. Density should be reduced first to activate the gravitational forces. Otherwise, any attempt for wettability alteration should solely rely on activating the capillary force, which is impractical at the field scale. Evaluation of the interplay of capillary forces and gravity forces under the effect of temperature should also be considered if the wettability is to be altered by thermal means. Babadagli (1996) observed that capillary imbibition can be enhanced at elevated temperature as a result of viscosity reduction.

In summary, to produce oil from oil-wet reservoirs, the following systematic steps can be followed:

1. Establish the mechanisms that shifted the wettability to oil-wet.
2. Determine the reservoir and fluids characteristics (current status of wettability, size of the reservoir, vertical continuity, fluid densities and viscosities, etc.).
3. Study the interplay between different forces under reservoir conditions (capillary, gravity and viscous force).
4. Determine which properties to be changed (viscosity, density, wettability, etc.).
5. Screen wettability alteration methods based on the reservoir rock type (sandstone, limestone, etc.) and the mechanism that had changed the reservoir wettability.
6. Optimize the parameters of wettability alteration.

6. Chemically induced wettability alteration

6.1- Surfactants. The main function of surfactant solutions is to reduce the interfacial tension between oil and water from moderate to ultra-low values. When mixed with oil and water, they form a micro emulsion of different types depending on the solubility of each phase on the other phase; i.e., Winsor phase behavior, which was defined by Winsor (1954) describing different types of micro emulsions that result when salinity is varied in an oil/water /surfactant system. These two characteristics are the major factors that play a role in enhanced oil recovery.

In addition to those, surfactants contain a hydrophobic tail and a hydrophilic head that can be positive (cationic surfactant) or negative (anionic surfactant). Nonionic surfactant has no charge. Depending on their spreading on the surface that is controlled by these charges and the charges of the rock surface, they may alter wettability. Surfactant flooding in oil-wet reservoirs is expected to serve both purposes: wettability alteration and IFT reduction. Two mechanisms of wettability alteration normally cited are removal of the oil-wet layer to expose the underlying originally water-wet surfaces or setting up a water-wet layer on the top of the oil-wet layer (Standnes and Austad, 2000). IFT reduction weakens the adhesive forces that retain oil by capillarity while wettability alteration activates capillary imbibition of water. Morrow and Mason (2001) stated the ratio of gravity forces to capillary force is of great importance and that lowering IFT may have a positive or negative effect on imbibition. While lowering IFT reduces the capillary imbibition, imbibition can occur as a result of gravity forces. Furthermore, wettability alteration may still be able to overcome the passive effect of IFT reduction (Spinler et al., 2000). As long as IFT is not reduced below certain critical values, capillary imbibition can be initiated and maintained. A study by Hognsen et al. (2006) showed that the interplay between gravity and capillary forces depends greatly on the IFT value.

Consequently, surfactant flooding should be evaluated based on the reservoir characteristic, the appropriate parameters to be used including the type of surfactant, concentration, and expected range of IFT. Reservoir temperature, for example, may limit the range of applicable surfactant. Thermal stability tests should be performed as well as the aging tests to examine the precipitation rate of surfactant. Spinler et al. (2000) aged surfactants for up to 16 months during the screening test to select the most useful surfactants. Generally, stability surfactant solution should be tested at the application condition (Hirasaki and Zhang, 2004). Floating tests can also be considered as a screening test (Wu et al., 2008). This test is used to determine the ability of surfactant to change the wettability of rock surfaces by using oil-wet calcite powder with different surfactants. If the wettability of calcite is changed from oil-wet to water wet, it will float.

The most frequently used screening test is contact angle measurement. Contact angle study provide fast and efficient to screen the ranges of surfactants for their ability to change the surface wettability. After the screening test and narrowing down the suggested surfactants, original reservoir plug or outcrop saturated with oil is placed in an imbibition cell filled with surfactant solution and oil recovery is monitored over time. An advanced visualization technique can be used to view the distribution of fluids during the imbibition test (Chen et al., 2000). A plot of oil recovery versus time indicates two valuable pieces of information, namely the rate of the recovery and the ultimate oil recovery. Capillary imbibition effect can be noticed in early time and the effect of gravity forces is observed in later times (Chen et al., 2000).

In addition to the imbibition curves, other information that can be obtained from the imbibition tests is the visual evidence of the contribution of these phases. The production from top surface usually results from co-current buoyancy forces and oil recovered from the lateral faces indicates counter-current capillary imbibition (Hognsen et al., 2006). One of the limitations of the imbibition test is that oil recovery is not necessarily recorded at the correct time of production. Oil droplets that displaced out of porous medium may need additional time to detach from the core surface.

The application of anionic, cationic, and non-ionic in wettability alteration for sandstone and limestone was documented in literature at concentrations lower or higher than critical micelle concentration (CMC). Researchers found that C12TAB at concentrations equal (Golabi et al., 2012) or higher than CMC (Standnes and Austad, 2000) can alter the wettability of carbonates better than anionic surfactants. Note, on the other hand, that Wu et al. (2008) concluded that no obvious correlation is found between oil recovery and CMC. Standnes and Austad (2000) proposed ionic-pair interaction as the mechanism of wettability alteration by cationic surfactant type CnTAB (n is the carbon atom number). The degree of wettability alteration was based on two factors: CMC value and the hydrophobicity of cationic surfactant. The higher the CMC value of CnTAB, the higher it is ability to change the wettability. However, this is also conditioned by the degree of hydrophobicity, which is determined by the n value. Wettability alteration was associated with both conditions. For example, while C10TAB has a higher CMC, C12TAB was found to have a better ability to modify the wettability than C10TAB as it is more hydrophobic.

Another condition needed to activate capillary imbibition is the existence of relatively high IFT between water and surfactant. Temperature improves the wettability as it increases the rate of diffusion of surfactant monomers and micelles. Anionic surfactants generally do not have the ability to alter the wettability of calcite surfaces, even when a very low IFT is achieved. Oil recovery is typically low for this kind of system and is mainly due to bouncy forces. Salehi et al.

(2008) tested the same principle on sandstones. They found that anionic surfactant STEOL C330 can change the wettability of sandstones better than cationic surfactants. They concluded that ionic-interaction between anionic head group and positively charged basic materials that were adsorbed onto the sandstone surface is the mechanism of wettability alteration. Also, they also found that wettability alteration is improved by increasing the negative charge of anionic surfactants. Even with lower IFT, a surfactant with two negative charges on the head group (surfactin) causes a very fast improvement in oil recovery, which is attributed to higher performance of surfactin in terms of wettability alteration in comparison with STEOL CS 330.

Nonionic surfactants were observed to be unable to change the wettability of carbonate surfaces by Standnes and Austad (2000; 2003a) Nevertheless, Vijapurapu and Rao (2004) tested the ability of nonionic surfactant to change the wettability using contact angle with the Yates crude oil. Contact angle measurements showed that nonionic surfactants are able to reduce the advancing contact angle from 156° to 39°. It also has an effect on IFT (reduced from 29 to 0.19 dyn/cm). Golabi et al. (2009) demonstrated that nonionic surfactant Triton X-100 has higher ability to change the wettability of carbonate than cationic and anionic surfactants. They also noticed that increasing temperature and increasing concentration improves the process of wettability alteration. An earlier study by Xie et al. (2004) also documented that nonionic surfactants are more efficient in wettability alteration. Most of the recovered oil occurred as a result of capillary forces and the production by gravity forces is insignificant. The better performance is attributed to the higher IFT that can be acquired with nonionic surfactant.

Wettability alteration by surfactants seems to be a slow process, yet is effective in reaching considerably high oil recovery. However, up scaling the results of many wettability alteration studies shows that spontaneous imbibition process, which takes months in the lab, might require several hundred years at the field scale (Stoll et al., 2008). Hence, the limitation of surfactant diffusion may threaten the feasibility of wettability alteration. One factor that can accelerate the process is temperature; however this implies additional cost to the process. To reduce the cost surfactants, researchers tested many commercial surfactants. Standnes and Austad (2003b) found that commercial-cheap surfactants can alter the wettability of carbonate samples as efficient as C12TAB as they have the same effective material.

One of the major challenges of surfactant flooding application in oil reservoirs is their adsorption on the rock surfaces. The effect of the type of the rock surfaces (carbonate/sandstone) on the adsorption of cationic and anionic surfactants is still a controversial issue. A study by Tabatabal et al. (1993) on the adsorption of cationic and anionic surfactants on sandstone and carbonate rocks reported that the adsorption of cationic surfactants on carbonates is less than the anionic

surfactants of similar hydrophilic chain length. This can even be further decreased by the addition of multi divalent ion. Addition of alkaline was observed to reduce the adsorption of anionic surfactants on carbonate surfaces significantly as stated by Seethepalli et al. (2004). They showed that at higher pH values, carbonate surfaces' charge reverted from positive to negative, leading to an increasing repulsive force between carbonate surface and anionic surfactant. On the other hand, Spinler et al. (2000) suggested that anionic surfactants may have low adsorption on chalk surfaces. Generally, there is an agreement that adsorption increases as surfactant concentration increases, reaching a maximum at the CMC value (Spinler et al., 2000; Seethepalli et al., 2004).

As seen, wettability alteration by surfactants is mostly tested for light oil and the application of surfactants on heavy oil is rare. Babadagli (2002) tested the imbibition of surfactant into limestone cores saturated with heavy oil. A positive effect in ultimate oil recovery was observed but the recovery rate was negatively affected. This was expected as surfactant reduces the IFT and capillary forces consequently. However, the increase in recovery was minor and the application of surfactant for such conditions deemed economically unfeasible. Addition of alkaline may improve the efficiency of surfactant flooding in heavy oil reservoir by emulsification of heavy oil in formation brine (Liu et al., 2006a).

6.2- Alkaline-anionic surfactant mixtures. As explained, anionic surfactants are not as efficient as cationic surfactant in carbonates for wettability alteration. For example, propoxylated ethoxylated surfactants (POEO) do not alter the wettability of carbonate surfactant and the acquired IFT is very low (Standnes and Austad, 2000). Ethoxylated surfactants (EO-sulfonates), on the other hand, induced higher IFT and were able to decrease the contact angle to values below 90°. However, wettability alteration was not efficient. Other anionic surfactants that were tested did not induce any wettability alteration (Staness and Austad, 2000). Addition of alkaline at optimal salinity was observed to improve the ability of anionic surfactant rendering carbonate surfaces more water-wet (Hirasaki and Zhang, 2004; Seethepalli et al., 2004; Zhang et al., 2006; Adibhatla and Mohanty, 2008; Gupta and Mohanty, 2011). Unlike cationic surfactants, the concentration used in alkaline-anionic systems was reported to be far below the CMC. The presence of alkaline in the system reduces the adsorption of anionic surfactant. In two different studies by Tabataba (1993) and Seethepalli et al. (2004), Na_2CO_3 was observed to minimize the adsorption of anionic surfactant on carbonate surfaces. Another advantage of using alkaline with anionic surfactant is the generation of in situ surfactants by alkaline. These surfactants are believed to dissolve naphthenic acids that had adsorbed in the carbonate surfaces (Hirasaki and Zhang, 2004; Gupta and Mohanty, 2011).

Na_2CO_3 is the most frequently used chemical in alkaline anionic surfactant systems as the CO_3^{-2} group reduces the positive charges on carbonates and thus, the adhesion of negatively organic

acids to the rock surfaces is weakened (Hirasaki and Zhang, 2004). Different alkaline anionic surfactant systems were also tested. For example, ethoxylated and popoxylated anionic surfactants such CS-330 and TDA-4PO at low concentrations (~0.05 %), when mixed with Na_2CO_3 were able to change the wettability of carbonate surface surfaces (Hirasaki and Zhang, 2004). The ethoxylated anionic surfactants that were tested by Gupta and Mohanty (2011) showed potential ability to alter the wettability of oil-wet carbonate surfaces. They were observed to improve this process when the ethoxylated group (EO) increases (Staness and Austad, 2000; Gupta and Mohanty, 2011). Other researchers stated that CS-330 is too hydrophilic and therefore it was mixed with another anionic surfactant (Zhang et al., 2006). The mixture of anionic surfactant at optimal alkaline salinity reduced water contact angle with time from 180° to $(80-140^\circ)$.

In certain cases, alkaline anionic surfactants provided a better performance than cationic surfactants as revealed by Seethepalli et al. (2004). They showed that alkaline (Na_2CO_3) anionic surfactant (Alfoterra) system solution is able to induce higher reduction in water receding contact angle than cationic surfactant DTAB. Note that concentrations that are usually applied in alkaline anionic surfactant systems are below or slightly above CMC concentration (Zhang et al., 2006; Seethepalli et al., 2004; Zhang et al., 2006). Although IFT reduction decreases the ability of alkaline anionic surfactant to imbibe by capillary forces, the buoyancy forces tend to compensate this effect as explained by Hirasaki and Zhang (2004) and Morrow and Mason (2001). Using a narrow gap that created from oil-wet microglasses and saturated with crude (Zhang et al., 2006) illustrated that alkaline anionic surfactant solution can displace the oil by water by spontaneous imbibition.

One of the important factors on designing a successful alkaline anionic surfactant system is optimum salinity. Selecting an alkaline concentration that provides the best solubility of crude oil reduces the total cost and maximizes the efficiency of wettability alteration by alkaline anionic surfactant mixtures. The optimal salinity may be determined using the phase behaviour test (Seethepalli et al., 2004; Hirasaki and Zhang, 2004), or by IFT measurement. Once the optimal salinity is determined, other electrolyte such NaCl can be used to enhance the electrical strength of the system (Hirasaki and Zhang, 2004). Other factors such as tolerance of alkaline to the water hardness should also be carefully considered. NaBO_2 for example has higher tolerance of water hardness than Na_2CO_3 . The selected published studies on wettability alteration by surfactants and alkaline surfactants mixtures are summarized in **Table 1**.

Table 1: A selection of published studies on wettability alteration by wettability alteration by surfactants and alkaline surfactants mixtures.

Surfactant type	Materials	Synthetic brine	Tests	Estimated final oil recovery ranges	General comments	Reference
C12TAB 0.6-3.5 wt. %	Outcrop Chalk	Sea water	Imbibition	50-90%	- Light oil -Observed the oil production from different surfaces of the cores. -Compared the contribution of gravity and capillary forces	Høgenesen et al., 2006
-Surfactants of the type tetra alkyl ammonium -Anionic Surfactant 0.1 wt. %	Outcrop Chalk	3 Brines with different content of dissolved solid(Na^+ , K^+ , Mg^{+2} , Ca^{+2} , Cl^- , SO_4^{2-} , HCO_3^{-1})	-Contact angle -IFT -Imbibition	10-75 %	-Light oil -(4 days-1 month)aging -Imbibition with Cationic > anionic -Tests run under different temperatures (40-70°C) Surfactant Concentrations > CMC	Standness and Austad, 2000
C(10-12)-amine 1.0 wt. %	-Outcrop chalk -Dolomite reservoir cores	2 Brines with different content of dissolved solid (Na^+ , K^+ , Mg^{+2} , Ca^{+2} , Cl^- , SO_4^{2-} , HCO_3^-)	- IFT. -Contact angle -Imbibition	50-75 %	-60 % Crude and 40 % Heptane -C12 –amine insoluble and is not a wettability modifier -C-10 amine can change the wettability at low temp but not at high temperature	Standnes and Austad, 2003
C12TAB , 1.0 % wt.	Outcrop Chalk	Brines with NaCl , NaHCO_3 , KCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ And Na_2SO_4 , KSCN	Imbibition	20-60%	-60 % Crude and 40 % Heptane -Temperatures ranges (90-130C) - Ion pair interaction as a wettability alteration mechanism mechanisms	Strand et al., 2006
C12TAB,C14TAB, C16TAB Alkyl Propoxy Ethoxy Sulfate(Mixture of anionic and nonionic)1.0 % wt.	Outcrop Chalk	Synthetic formation brine (NaCl , Na_2SO_4 , NaHCO_3 , KCl , MgCl_2 , CaCl_2)	-IFT -Imbibition test	50-70%	-60 % Crude and 40 % Heptane -C12TAB changes wettability of chalk	Austad a et al., 1997
CTAB and Ethoxylated sulfonates 1 wt. %	Short and long outcrop Chalk	Synthetic brine	-Imbibition test	50-70%	-Crossover in the imbibition mechanism from capillary-dominated flow at 70° C to more -Gravity-dominated flow at 40° C in long cores	Austad and Standnes, 2002
C12TAB 1.0 % wt	Outcrop Chalk	Brines (Na^+ , K^+ , Mg^{+2} , Ca^{+2} , Cl^- , SO_4^{2-} , HCO_3^-)	-Imbibition test	50-85%	-Aging 4 weeks at 90° C -Temperatures ranges (40-130°C) -Temperature is a crucial factor for Sulphate to be effective as well as ($\text{Ca}^{+2} / \text{SO}_4^{2-}$) concentration ratio	Austad et al., 2005
Anionic surfactant (n-dodecyl-o-xylene-sulfonate) (0.001-0.1 wt.%)	Berea Sandstone	Brine 1.5% NaCl	imbibition	S_{or} reduced down to 0%	-Light oil : Heptane - As surfactant concentration increases. the residual oil decreases and the wettability is changed to neutral then oil wet	Alveskog et al., 1998
Anionic surfactant(Alkyl – propoxy-ethoxy-sulphaste) and Cationic surfactant(CTAB) 1.0 wt %	Chalk core plugs	Synthetic brine	Phase study	60-70%	-Light oil : Heptane -Cationic surfactant is able to change the wettability of oil wet chalk , The wettability mechanism provided in these paper (reverse micelle formation) is revised by the author in the recent papers	Austad, and Milter, 1997

Surfactants of the type R-N(CH ₃) Arquad Dodigen 1 wt. %	Dolomite and Chalk core samples	Low and high salinity brines	IFT Contact angle Imbibition	70-90%	-60 % Crude and 40 % Heptane -Arquad and Dodigen surfactant is able to change the wettability of carbonate Recovery is more from dolomite cores compared to chalk. -As temperature decreases , recovery is more influenced by gravity	Austad and Standnes, 2003
-Anionic surfactant (Ethoxylated sulphonate) CTAB,DTAB, Aaqud -Non-ionic, ethoxylated Concentration < 0.2 wt. % Cationic and non-ionic	Limestone	Formation brine(NaCl,MgCl ₂)	Contac angle Imbibition test	70-80%	-Aging (1-2 months) -Mixture of cationic and non-ionic is stable at high Temperature and high salinity and can be effective in wettability alteration of carbonate	Sharma and Mohanty, 2011
Anionic surfactant and Sodium carbonate mixture 0.05-0.1 wt. %	Dolomite	Formation brines(NaCl, KCl,CaCl ₂ ,MgCl ₂ ,Na ₂ SO ₄)	Contact angle Imbibition test Displacement in narrow gap	40-50%	The wettability of calcite can be changed by Anionic surfactant and Na ₂ CO ₃ or NaHCO ₃	Hirasaki and Zhang, 2004
Non-ionic ethoxy alcohol surfactant < 3500 ppm	Dolomite	Synthetic brine Actual reservoir brine (Cacl ₂ ,MgCl ₂ ,Na ₂ SO ₄)	Contact angle	-	Non-Ionic surfactants can decrease the contact angle from 156 ° to 39° degree.	Vijapurapu and Rao, 2004
-Cationic surfactant (C12TAB) and an anionic surfactant (STEOL CS-330) bio surfactant, -Surfactin Immole/l	Sandstone cores Synthetic cores	Synthetic brine (10 g/L NaCl), 1.0 % Deionized water	-IFT -Imbibition test	10-30%	-Light oil (5 cp) -Aging at 90 C for 1 month - Anionic surfactant changes oil wettability of wet sandstone by Ion-pair exchange) - Electrostatic interaction Increases when increase the negative head group increases -Dimeric surfactants might be effective for sandstone	Salehi et al., 2008
Anionic and Non-ionic surfactants 0.1 wt. %	Calcite plates Limestone core	Na ₂ CO ₃ and NaCl	-IFT -Phase behavior -Contact angle -Imbibition test	60-75%	-Light oil (24cp) -Temperatures ranges (25-90°C) Temperature increase the effect of anionic and non-ionic surfactant -Gravity driven process	Gupta and Mohanty, 2010
Anionic surfactants (Sulfate and Sulfonate) 0.1-.5 wt. %	Calcite plates Limestone core	Synthetic brine (Na ₂ CO ₃ , NaCl Na ₂ SO ₄ , CaCl ₂ , and MgCl ₂)	-IFT -Contact angle -Imbibition test	30-50%	-Light oil (24 cp) -Imbibition testes was run at high Temperature (90°C) - Optimum surfactant concentration directly linked with brine salinity - Anionic surfactants desorbs the naphthenic acid from carbonate surface when mixed with NaCO ₃ (calcite charge is switched from positive to negative charged at high pH) -	Gupta and Mohanty, 2011
Anionic surfactant Ethoxylated (EO) and propoxylated (PO) sulfates 0.05-wt%	Calcite plates Marble plates	Sodium chloride is used along with 1% sodium carbonate	-IFT -Phase behavior -Contact angle -Imbibition test in narrow gap	60-90% (Narrow gap)	-Problems with IFT measurements for alkaline anionic surfactant systems -Adsorption of anionic surfactant decreases with addition of sodium carbonate -Adsorption of anionic surfactant decreases when flow rate decreases -Alkaline anionic surfactant is able to alter the wettability of carbonate	Zhang et al., 2006

Anionic Ethoxylated (EO) and propoxylated (PO) sulfates and cationic (CTAB) 0.05-wt.%	Calcite (Iceland spar), lithographic limestone, marble, and dolomite plates were	Synthetic brine (Na ₂ CO ₃)	-IFT -Phase behavior -Contact angle -Imbibition test	35-55%	-Light oil (20 cp) -Anionic surfactant in presence of Sodium carbonate is able to change the calcite wettability of carbonate from oil-wet similar or even better than cationic - Adsorption of anionic surfactant decreases when sodium Carbonate is added to the system	Seethepalli et al., 2004
Cationic surfactant(CAC) and non-ionic surfactant Ethoxylated alcohol 75-2600 ppm	Dolomite cores	Synthetic brine (Na ₂ CO ₃)	-IFT -Imbibition test	5-15%	-Light oil(25 Cp) -Aging (10 days) at (55-60°C) -Surfactant concentration slightly above CMC - Non-ionic performance is better than cationic for wettability alteration of carbonate and faster recovery is achieved (the effect of high IFT)	Xie et al., 2005
-Nonionic ethoxyl alcohol 3500ppm -Anionic ethoxyl sulfate 3500ppm	Yate reservoir core (limestone and dolomite)	Yates field synthetic brine	CT scan imbibition	40% increase in oil recovery compare to brine	-Light oil (13 cp) -Aging with oil : 6 weeks -Surfactant concentration above CMC -Both non-ionic and anionic change the wettability to moderately oil wet state but not water wet. -Oil is produced because of the capillary at early time and gravity effect is dominated at late time	Chen et al, 2001
Anionic surfactant : Ammonium salt of ethoxylated and sulfated alcohols (C8-C10 alkyl ethers) 300-3000ppm	Outcrop chalk Reservoir chalk plugs	North sea water	IFT imbibition Flooding	Up to 24%	-Light oil -When the concentration of surfactant is below CMC the adsorption decreases -Surfactant stability can be measured through cloud points and onset of precipitation	Spinler et al., 2000
Anionic surfactant n-dodecyl-o-xylylene-sulfonate (0.001-0.1 wt.%)	Berea Sandstone	Brine 1.5% NaCl	imbibition	S _{or} down to 0%	-The oil was n-heptane - As surfactant concentration increases. the residual oil decreases and the wettability is changed to neutral state.	Alveskog et al., 1998
Commercial surfactants	Berea Sandstone	Deionized water	IFT	50-70%	-Oil was Decane -imbibition can occur in three different regimes: *Capillary-dominated *Gravity-dominated *Intermediate regime where both forces affect Imbibition. -Reduction of IFT for imbibing fluids may increase or decrease imbibition rate, depending on the relative contribution of capillary and gravity forces.	Al-Lawati and Saleh, 1996
C12TAC 0.01 to 0.5 wt.%	heavy oil-impregnated calcite cores	Water	-Molecular modeling -Imbibition tests	35-44%	-Heavy oil and light oil -C12TAC might change the wettability of cores contain light oil not heavy oil -C12TAC was not able to detach asphaltene and resin for carbonate surface	Jiménez et al.,2014
Two anionic and two non-ionic (0.2, 1 and 2 gallons per Thousand gpt)	Siliceous and carbonate shale cores	Water	Contact angle Imbibition tests		-Anionic and non-ionic surfactants have the ability to change the wettability of carbonate shale reservoirs - Anionic surfactant showed better oil recovery from shale than non-ionic	Alvarez et al., 2014

6.3- High pH solutions. Early studies showed that alkaline flooding in sandstones can increase oil recovery (Ehrlich and Wygal, 1977; Leach et al., 1962). Many mechanisms were suggested including wettability alteration and the formation of in situ- surfactants as a result of alkaline

reaction with acids in crude oil. Ehrlich and Wygal (1977) showed that alkaline flooding using NaOH solution improves oil recovery for crudes oils with acid numbers more than 0.1-0.2 mg KOH per gram of oil. Relative permeability measurements indicated that wettability of Berea cores is changed to be more water-wet after flooding with 1.25N NaOH solution. In only one crude oil among those tested, it was found that emulsification is responsible for improved oil recovery. In that sample, the acid number was considerably high (1.39 mg KOH per gram of oil). Calcites surfaces normally have positive charges at pH less than 9, which encourages the attachment of negative acidic components from crude oil to the carbonate rock surfaces and renders them oil-wet. Reduction of pH will decrease the positive charges on the calcite surface and consequently increase repulsive forces between the calcite surface and adsorbed organic components. Changing pH value was suggested as a mean to change the wettability of carbonate reservoirs. An experimental study by Zhang et al. (2008) investigated the effect of different high pH solution on carbonate reservoirs.

Contact angle measurements were performed on silica and carbonate plates using Na_2CO_3 and NaBO_2 solutions. While NaBO_2 did not reduce the contact angle significantly, Na_2CO_3 changed the wettability of both silica and carbonate from oil-wet to water-wet. On the other hand, natural imbibition tests using porous flat plates and short carbonate cores indicated that NaBO_2 caused stronger imbibition than Na_2CO_3 in spite of pH around 11.5 for both solutions. The performance of high pH solutions was better than surfactants and no improvement in the recovery was observed when NaOH was used.

The oil recovery mechanism by NaBO_2 was attributed to its high pH value and the tolerance of NaBO_2 to high cations concentrations. In their experimental study of alkali injection after water flooding in limestone, Najafabadi et al. (2008) showed that the wettability of limestone was changed from oil-wet to water-wet. Capillary forces were reverted from negative sign to positive sign. Oil was recovered by capillary forces and viscous forces. Spontaneous imbibition tests on siliceous shale indicated high pH solution had the higher efficiency in wettability alteration followed by low pH solution, whereas neutral pH solutions were not able to induce any wettability alteration (Takahashi and Kavscek, 2010a). Zeta potential measurements on siliceous shale (Takahashi and Kavscek, 2010b) also supported this result as it showed that aqueous film was not stable at neutral pH causing not-water water state. High pH solution was able to stabilize the water film and modified the wettability into more-water wet.

A field trial in the Harrisburg Muddy reservoir was conducted to test the possibility of using alkaline flooding to increase oil recovery by wettability alteration. Injection of 2% NaOH was carried in multiple wells followed by water injection. A gradually increased oil recovery was observed in many wells indicating that reservoir wettability was changed from oil-wet to water-

wet (Leach et al., 1962). They pointed out that conducting wettability alteration at early stages of water flooding in oil-wet reservoirs can reduce the residual oil to extent similar to that of water-wet reservoir. A selection of published studies on wettability alteration by high pH solutions are provided in **Table 2**

Table 2: A Summary of selected published studies on wettability alteration by high pH solutions

Alkaline	pH range	Rock type	Brine	Experiments tests	Results	Reference
NaOH-HCl (0.1-0.4molar)	-	Berea sandstone	-Fresh water -5500 ppm KCL -Formation brine	-Contact angle -Field test	-As NaOH increased contact angle reduced from (135°-170°) to (40°-70°) -Injection of NaOH altered the wettability of oil-wet Harriburge Muddy oil-wet formation to be more water-wet	Leach et al., 1962
NaOH 1.25 N	-	Berea sandstone	Water	Core flooding	-Light oil(API >30) -The wettability Berea sandstone was altered to be more water-wet after acoustic flooding -Higher clay content or acoustic consumption reduces the improved oil recovery by NaOH	Ehrlich and Wygal, 1977
NaOH-Na ₂ CO ₃ -NaBO ₂ (1-4.8 wt.%)	11-11.5	Texas cream limestone	Water Surfactants	-Dynamic contact angle -CT-Aided visualization of in-situ imbibition	-Light oil 36.2 API -NaBO ₂ showed higher potential to alter the wettability of carbonate than other alkalis -NaBO ₂ has highr tolerance to high divalent ions concentration in the brine	Zhang et al., 2008

6.4- Low salinity water. The injection of low salinity water (LSW) to increase oil recovery provides low cost EOR method. In their study about the effect of low salinity oil recovery by water flooding, Tang and Morrow (1997) showed that lowering the salinity of water resulted in enhanced spontaneous imbibition and increased oil recovery. Nasralla et al. (2013) also observed an improvement of oil recovery with low salinity water (LSW) injection. It is believed that wettability alteration is one of the effective mechanisms in this process (Morrow and Buckley, 2011). There has been a growing interest of the low salinity water in the recent years. Morrow and Buckley (2011) provided the recent bibliography in that area. They stated that the detachment of mixed wet fine particles (e.g., kaolinites) which are believed to be the cause of reversal wettability can be removed during LSW injection. Vledder et al. (2010) reported similar observations. Although pH was increased during the process of low salinity water injection due to ions change, they suggested that this was not the reason for increased oil recovery because IFT was high during

the process.

Berg et al. (2009) used open flow model geometry where drops of oil that attached to clay particle were displaced by low salinity water (TDS 2 g/l of NaCl and high salinity water TDS 25.95 g/l). The amount of oil that detached from the clay was significantly higher and was attributed to low salinity water, which weakened the adhesive force between clays and the drop of oil. Wickramathilaka et al. (2010) performed imbibition tests on limestone and sandstone cores using brine with different salinities. No effect of salinity water on the recovery was observed for limestone while LSW was effective in increasing the oil recovery from Berea sandstone and original reservoir sand. They also noticed a decrease in pH for reservoir sandstone cores. LSW was also tested at the field scale. Vledder et al. (2010) reported that 5-15% incremental oil recovery may be achieved in oil-wet sandstone reservoirs by LSW. The clay content of the reservoir was in the range of 0.5-4% and was mostly composed of kaolinites. LSW injected was from a river with the salinity about 500 mg/l.

Recent spontaneous imbibition tests for low, moderate, and high salinity water showed that both recovery rate and ultimate oil recovery were higher for LSW (Morrow and Buckley, 2011; RezaeiDoust et al., 2009). According to these authors, salting-in mechanism may be the main reason of wettability alteration in sandstones by LSW if clay is responsible for oil-wetting state. Salting-in refers to the process of reducing the salinity of water to increase the solubility of organic compounds (RezaeiDoust et al., 2009).

In addition to the mineralogy of sandstone, composition of oil (Nasralla et al. 2013) could play a role in wettability alteration by LSW. Alotaibi et al., (2010) and Alotaibi et al. (2010) reported that LSW was efficient in changing the wettability Berea sandstone but not the Scioto sandstone. These two types of rocks have different rock composition. Advanced oil contact angle measurements indicated that the wettability of the Scioto sandstone was not altered by LSW. On the other hand the same authors reported that LSW modified the wettability of Berea sandstone making it strongly water-wet. Surface charges were significantly affected by LSW injection. LSW resulted in a significant decrease in the Zeta potential of clay particles. Note that these experiments were performed in porous rock. Nasralla et al. (2013) suggested using mica for contact angle measurement for sandstones as it does not have the interference in the data (hysteresis) due to surface roughness.

Nasralla et al. (2013) evaluated the injection of different salinities from 0 mg/l up to 17400 mg/l in oil-wet sandstone using mica plates. The decrease in water contact angle measurements on mica showed that low salinity water can alter the wettability of mica surfaces. They stated that double

layer expansion is the main mechanism of wettability alteration. They also show that the composition of oil is an important factor. Zeta potential study showed that repulsive forces between oil and sandstone surface increases as the negative charges on the rock/brine brine/oil increases resulting in an alteration of wettability toward water-wet state. Core flooding on Berea sandstone confirmed this observation. Flooding with de-ionized water (DI) resulted in the highest oil recovery while the solution that had the highest salinity yielded the lowest oil recovery (Nasralla et al. 2013).

Double layer expansion was also suggested as the main mechanism for wettability alteration earlier by Vledder et al. (2010). Using oil-wet sandstone samples, they concluded that the high concentration of multi divalent ions in high salinity reservoir brine reduces the negative electrical charge on clays surface resulting reduction in repulsive forces. Thus, surface active materials in crude oil come into direct contact with clay making it oil-wet. Decreasing the amount of divalent ions by injecting low salinity water leads to the expansion of double layer and thus increases in repulsive force between crude oil and clay surfaces.

6.5- Smart water. Smart water refers to the process of customization water composition to serve specific applications. RezaeiDouset et al. (2009) used this term to describe the injection of sea water into chalk reservoirs. In wettability alteration, this term was used to indicate the injection of water with different brine properties to modify the wetting properties towards more water-wet. Quite a number of studies (Wanger and Leach (1959); Zhang et al. 2007; Yousef et al., 2012) showed that the modification of water composition, pH or salinity might lead to improved oil recovery by wettability alteration. Wanger and Leach (1959) concluded that the addition of simple chemicals such acids, basics, or salts may alter the wettability of petroleum reservoirs. As explained in the previous (LSW) section, the modification of injected water composition and salinity can have a positive impact on oil recovery in sandstones. Many studies observed similar results in carbonate reservoirs at different water composition (Strand et al., 2006; Zhang et al., 2007; Gupta and Mohanty, 2008; RezaeiDouset et al., 2009; Yousef et al., 2011; Yousef et al., 2012). While wettability alteration to more water-wet was observed generally in sandstones, these studies show that high salinity water is successfully used to improve the water-wetness in carbonates. RezaeiDouset et al. (2009) discussed the difference in wettability alteration mechanisms by smart water in sandstone and limestone. They explained the difference in wettability alteration mechanism based on the strength of adhesion force of adsorbed material in clays and carbonates. This force, they mentioned, is relatively strong in carbonates and salting-in effect that occurs during the injection of low salinity water is not efficient in modifying the surface properties. In sandstones, this adhesion force is relatively weak and low salinity water can lead to desorption of organic material from sandstone surfaces that rendered it oil-wet.

The composition of injected water for wettability alteration is usually customized based on the composition of multi-divalent ions such as calcium, magnesium, and sulfate ions. A study by Gupta and Mohanty (2008) shows that magnesium ions and sulfate ions are not efficiently able to change the wettability of carbonate surface. Calcium ions alone can change the wetting state of carbonate surface into more water-wet state and the efficiency is increased when both sulfate and magnesium ions were added to the solution. A study by Zhang et al. (2007) also showed that magnesium ion can substitute calcium ion. A more recent study by Sakuma et al. (2014) using molecular modeling suggests that this substitution in addition to the substitution of CO_3^{2-} by SO_4^{2-} reduces the adsorption of organic material on carbonate surface. In carbonate reservoir, high salinity water that contains multi-divalent ions, such as sea water, (Zhang et al., 2007; Strand et al., 2008a) changes the chemical equilibrium of crude oil-brine and rock system into more favorable water-wetting. A study by Strand et al. (2006) explained that when high salinity water is injected into carbonate reservoirs, the concentration of two determining ions increased calcium and sulfate. The result will be an increase in the adsorption of sulphate in rock surface.

Co-adsorption of calcium ion will also increase calcium ions concentration. Consequently, positive sites on carbonate surface will be minimized, repulsive forces between crude oil and carbonate surface will increase and carboxylic acid removed from carbonate surface by sulfate ion will lead to more water-wet state.

Recovery by spontaneous imbibition was 40% higher when sea water was used in compare with brine solution (Zhang et al., 2007; Strand et al., 2006; RezaeiDouset al., 2009). Sulphate ions in the formation brine in carbonate reservoirs are low because most of it precipitated as it reacts with calcium ions to form CaSO_4 . Note that high temperature was reported to be significantly important in this process (Zhang et al., 2007; Gupta and Mohanty, 2008; Strand et al., 2008b). The importance of sulfate ion was tested by Strand et al. (2008) who found that oil recovery by multi-divalent ion solutions is reduced 15% when sulfate ion was not included in the composition. Contact angle measurement and NMR study conducted by Yousef et al. (2011) suggested that contact angle is more affected by the composition of injected water than IFT. Yousef et al. (2012) revealed that smart water flooding in a field scale trial is able to reduce the residual oil saturation about 7 units in comparison with conventional sea water injection. A summary of selected published studies on wettability alteration by low and high salinity water is given in **Table 3**.

Table 3: A selection of published studies on wettability alteration by low and high salinity water

Wettability modifier	Materials	Brines	Tests	Range of recoveries	Results	Reference
Low salinity water	Oil-Mixed wet sandstone reservoir	River water , Salinity 500 mg/l ,bivalent cations << 100mg/l	-SCAL,NMR Log -Core flooding	5-15 %	Light oil 0.3 cp Reasons why sandstone might exhibit an oil wet behavior	Vledder et al., 2010
Low salinity water	Outcrop sandstone	Brine composition(Na ⁺ , Ca ²⁺ ,Cl ⁻)	-Imbibition test	50—75%	Light oil (17 cp) Aged at 60 for two weeks	Austad et al., 2010
Low salinity water	Berea sandstone core plug	Brine with salinity < 5000 ppm	-Imbibition test	20-40 %	-Provided in wettability alteration by LSW -Identified the conditions necessary for LSW	Morrow and Buckley, 2011
Low salinity water	Berea sandstone core plug	Brine salinities vary with different TDS concentration	-Imbibition test -Core flooding	10-75%	-Light oil(300cp) -Swi established for all cores -Wettability towards water wetness is increased as temp increases	Tang and Morrow, 1997
Low salinity water	Reservoir sandstone core	-Synthetic reservoir brine -Synthetic sea water brine Composition (Na ⁺ , K ⁺ ,Mg ⁺² , Ca ²⁺ ,Cl ⁻ , SO ₄ ²⁻ ,HCO ⁻)	-Imbibition -Core flooding	50-75%	- Light oil (70 cp) -Swi and presence of clay particles are essential factors for Low salinity T=55° C	Tang and Morrow, 1999
Low salinity water	Mica minerals Berea sandstone	Brines with different compositions of (Na ⁺ , K ⁺ ,Mg ⁺² ,CaSr,Cl ⁻ , SO ₄ ²⁻ ,HCO ₃ ⁻)	-Contact angle -Core flooding	8-22% improvement in recovery	-Light oil (20-30 cp) -Change in electric charges at CBR interfaces causes the wettability alteration	Nasralla et al., 2013
Low salinity water	sandstone core plug	Brine composition (NaCl,KCl,CaCl ₂ , MgCl ₂)	Flow cell	Up to 80 %	-The effect of clay and - Clay swelling -Mechanism of wettability alteration -Low salinity can cause formation damage	Berg et al., 2009
Low salinity water	Mica plates	Brines with different pH and salinities	Contact angle Zeta potential	-	-Double Layer Expansion was found to be the mechanism of oil recovery by low salinity water -Reducing pH suppresses the ability of low salinity water to change the wettability from water-wet to oil-wet	Nasralla and Nasr-El-Din, 2014
Divalent ions (Mg ⁺² ,Ca ⁺² , and SO ₄ ⁻²)	Indiana limestone cores	Cationic and Non-ionic surfactants	Imbibition tests	Up to 60%	-0.01M of SO ₄ ⁻² or Ca ⁺² lead to oil high recovery in carbonate - Mixture of non-ionic and cationic surfactants in high salinity brine improves the oil recovery	Dakik and Gupta, 2014
Sea water	Outcrop Chalk	Two modified reservoir brines Synthetic -Seawater -Brine with potential determining ions (Ca ²⁺ ,Mg ²⁺ , and SO ₄ ⁻²)	-Imbibition -Core flooding	20-65 %	-60 % Crude and 40 % Heptane -Temperatures range (70-100-130° C) -The presence of Ca ²⁺ , Mg ²⁺ , and SO ₄ ⁻² can change the wettability but needs high temperature	Zhang et al., 2006

6.6- Nanofluids. Nanofluid is designed by dispersion of nanoparticles in base fluids (Yu and Xie, 2011) and nanoparticles with size less than 100 nanometer (nm) have been applied in different aspects of oil industry. For example, when mixed with heavy oil, metal nanoparticles reduce viscosity (Shokrlu and Babadagli, 2010). Nanofluids can be customized according to the specific application and are characterized by the size and concentrations of nanoparticles and the wettability of these particles. Nanoparticles could be either hydrophilic or hydrophobic based on the functionalized group. Nanofluid is also characterized by the properties of the suspending fluid such as chemical composition and pH value. The suspending fluid can be water (Onyekonwu et al., 2010; Hendraningrat et al., 2013), brine (McElfresh et al., 2012), or surfactant solution (Karimi et al. 2012a; Geraldo, et al 2013).

6.7- Preparation. Different methods that are used to prepare nanofluids have been well documented in literature. One- or two-step methods are the most frequently cited. In the two-step method, a dry powder of nanoparticles is created first and then nanoparticles are dispersed in a suspending fluid using ultrasonic vibration or strong shear mixing. Yu and Xie (2011) provided a review on a number of nanofluids preparation methods.

6.8- Stability. Stability is nanoparticles dispersion is one of greatest challenges of nanofluids application in oil industry. To achieve homogenous stable nanofluid, different techniques are applied including addition of nonionic surfactants (Karimi et al. 2012a), anionic surfactants (Giraldo et al., 2013), surface modification (Yu and Xie, 2011), and using ultrasonic vibration (Williams et al., 2006).

Williams et al. (2006) used ultrasonic vibration (+12 hours) to prepare nanofluids using zirconium and alumina nanopowder. The prepared nanofluids were observed to be unstable and most of the particles were agglomerated. To increase the stability of the nanofluids, an “energy barrier” was generated using two mechanisms: (1) By maximizing either electrostatic or steric repulsive force over attraction forces and (2) by modifying pH by adding HCl acid, which enhances the electrostatic repulsive force and lead to more stable nanofluid when accompanied with ultrasonic vibration. Williams et al. (2006) and Safari and Jamialahmadi (2013) used surfactants to enhance the steric repulsive forces. The efficiency of surfactant in the stabilizing nanofluids is controlled by the dielectric constant; high and low dielectric constants are more efficient than moderate constants. Wamkam et al. (2011) provided a relationship between the Zeta potential and pH with the average particle size (nm). To obtain the lowest particle size the pH of the solution has to be at the maximum or the minimum pH value. The lowest values of average particle size can be found at the highest and the lowest pH value and the Zeta potential. Shokrlu and Babadagli (2014) used

Xanthan gum polymer to stabilize nickel nanoparticles. They conducted a micro model visualization experiment using nickel nanoparticles with and without this type of polymer. When no polymer was added to the solution used to inject nanoparticles, they were not stable and trapped in the model. Surfactants were also tested as a suspending agent but they were not able to stabilize the nickel nanoparticles.

6.9- Wettability alteration. Silica nanofluid in water solution was able to decrease the contact angle from above 100° down to 0° (Maghzi et al., 2012). This is achieved by the adsorption of nanoparticles that have an affinity to rock surface during the injection of nanofluids into porous medium. A study by Onyekonwu et al. (2010) examined the effect of lyophobic and hydrophilic polysilicon nanoparticles (LHPN of 20-60 nm) on oil recovery from water-wet sandstones. Water was used as a suspending fluid. Interestingly, a negative effect of using LHPN on water-wet sandstone was reported and increasing the water-wetness of the water-wet core decreased oil recovery. Core flooding experiments also indicated that permeability is affected negatively by this type of nanofluid. The visualization of the color change of the injected nanofluid from cloudy to colorless demonstrated that most of nanoparticles had been adsorbed on the rock surface and damaged the rock permeability (Onyekonwu et al., 2010). On the contrary, the LHPN did have a positive impact on oil-wet reservoir carbonate as it was able to alter the wettability to be more water-wet, more oil was recovered consequently.

Nanofluids increase the oil recovery by reducing the IFT and changing the wettability. McElfresh et al. (2012) stated that nanoparticles arrange themselves in wedge form (**Figure 4**) referring to an earlier study by Wasan and Nikolov (2003) that explained the mechanism of removing oil from soil by nanofluid. The wedge-like structure enhances the ability of nanoparticles to displace the oil phase from the rock surface.

McElfresh et al. (2012) used stabilized nanoparticles dispersion (NPD) of silica nanoparticles (4-20) nm in imbibition tests using sandstone cores. The result indicated that both NPD 10% solution and brine solution yield the same ultimate oil recovery. However, a faster recovery was observed with 10% NPD. Core flooding in sandstones and limestone showed an improvement in oil recovery after silica NPD injection.

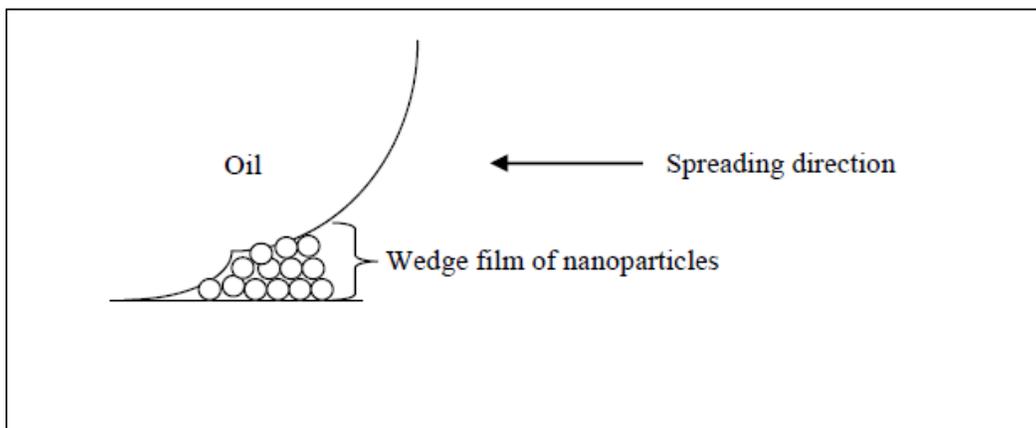


Figure 4: Wage film of nanoparticles displacing crude oil from a solid surface (reproduced after McElfresh et al., 2012 and Wasan and Nikolov, 2003).

The application of nanofluids in wettability alteration is relatively new. A number of studies showed that nanoparticles dispersions can alter the wettability of oil-wet carbonates (Karimi et al., 2012) and sandstones (Giraldo et al., 2013; Ju and Fan, 2009). When hydrophilic nanoparticles adsorb on the rock surface, a thin nanotexture is formed, coating the rock surface. As a result, wettability of the surface becomes more water-wet (Karimi et al., 2012a; Maghzi et al., 2012; Giraldo et al., 2013). Alumina, silica, and zirconium nanofluids were found to have significant effect in changing the characteristic of sandstone and carbonate. Ju and Fan (2009) tested the effect of lipophobic and hydrophilic polysilicon nanoparticles (LHPN) on wettability of oil-wet sandstone rock slices. They found that LHPN could alter the wettability of sandstone toward water-wetness. Maghzi et al. (2012) used micro model to study the effect of silica nanoparticles on the wettability alteration. After aging glasses in crude oil for 40 days, contact angle measurements were performed and indicated that surfaces of glasses became oil-wet. A dispersed silica nanoparticles in water solution was able to decrease the contact angle from above 100° down to 0° . The ultimate oil recovery by silica nanofluid increased substantially and the suggested mechanisms was the adsorption of silica nanoparticles on the oil-wet surfaces. The adsorption of silica nanoparticles reduced silica-oil surface tension and thus decreased contact angles (Maghzi et al., 2012).

Karimi et al. (2012a) tested studied the spontaneous imbibition of zirconium nanofluids into oil-wet carbonate plugs. Zirconium nanofluids were composed of zirconium nanoparticles that dispersed in the mixture of nonionic surfactants at 5wt %. The concentration of zirconium nanoparticles was 0.05 gram /cc and the pH value ranged from 2 to 3. The contact angle of n-heptane/water for oil-wet carbonate rocks showed that zirconium nanofluid can reduce the water contact angle significantly, which implies that zirconium can reverse the wettability of carbonate surface. Spontaneous imbibition tests were also carried out using oil-wet carbonate core samples.

It was demonstrated that up to 60% OOIP can be recovered during spontaneous imbibition of zirconium nanofluids in comparison to less than 5% OOIP by distilled water. Spontaneous imbibition tests were performed at 70°C but the effect of the temperature on the process was not analyzed. Apparently, the surfactant also contributed to the recovery but spontaneous imbibition of surfactants without nanoparticles was not performed to quantify this effect. Finally, Karimi et al. (2012a) developed a theoretical model to explain the change in wettability by nanofluids. They concluded that nanofluid can form smooth surfaces with neutral wettability.

Safari and Jamialahmadi (2013) conducted contact angle measurement using above mentioned LHP nanofluid with 14 nm size (0.05-0.1 wt %) and pH ranged from 3.7 to 4.7. Results indicate that carbonate rock surfaces altered to be more water wet by LHP nanofluid. Alumina nanofluids were tested by Giraldo et al. (2013). They revealed that alumina nanofluids can enhance the ability of surfactant to change the wettability of oil-wet sandstone as it adsorbs on rock surface and cover oil-wet surfaces.

Displacement tests for secondary and tertiary recovery were also performed by many studies. For example, Hendraningrat et al. (2013) tested LHP silica nanofluids for oil-wet and intermediate water-wet sandstones. The core flooding tests indicate that wettability was altered by LHP silica nanofluid. After water flooding, the cores were flooded with nanofluids. Incremental oil recovery was higher for intermediate water-wet core; the same core achieved the lowest recovery after water flooding. They also found that it increased the recovery and that increasing the flow rate decreased the recovery. Hendraningrat et al. (2013) found that decreasing the size of the particles enhances the recovery. The highest oil recovery was achieved at 7nm size indicating that the optimization of nanofluid should consider decreasing the size of nanoparticles to a minimum. No adverse effects on permeability were observed.

Silica nanoparticles can be used for wettability alteration and for improving the water injectivity. Ju et al. (2012) used water-wetting control agent that is designed by nanometer scaled powder formed mainly from silica nanoparticles. This was able to decrease the water contact angle indicating wettability alteration. Zhang et al (2014) showed that hydrophilic silica nanoparticles (19nm) can imbibe into Berea sandstone core displacing about 55% of oil in place. De-ionized water recovered less than 5% after two weeks of imbibition tests on the same type of core sample.

A selection of published studies on wettability alteration with nanofluids is presented in **Table 4**.

Table 4: Selection of published studies on wettability alteration by low nanofluids

Nanoparticles type and concentration	pH range	Size (nm)	Materials	Brine	Tests	Results	Reference
Zirconium oxide (0.05 grams/cc)	2-3	24	Oil-wet carbonate core	Nonionic surfactants	Contact angle Imbibition SEM	-Mixture of kerosene and 425cSt at 25 ^o C -SEM showed the adsorption of ZrO ₂ nanoparticles on the surface is slow process -Contact angle and imbibition tests indicated the ability of ZrO ₂ to alter the wettability of carbonate	Karimi et al., 2012a
Alumina oxide (100-10000 ppm)	9.3	35±4	Oil-wet sandstone core Oil-wet sand pack	Anionic surfactants	Contact angle Imbibition	-Reduce water contact angle from 142 ^o to 0 ^o -At concentrations lower than 500 ppm , alumina nanoparticles enhances the ability of surfactant to alter the wettability of sandstone	Giraldo et al., 2013
Silica nanoparticles (0.1-5.0) wt.%	-	14	-Glass -Micro model	Distilled water	Contact angle Core flooding	-Adsorption of silica nanoparticles increased when concentration was increased -Silica nanofluid altered the wettability of oil-wet glass from oil-wet to water-wet	Maghzi et al., 2012
Modified Silica nanoparticles 10%	-	4-20	Berea sandstone Indiana limestone	Water	SEM Imbibition Core flooding	-SEM showed the adsorption of silica nanoparticles at the interface -Faster imbibition of silica nanofluid in compare with brine -Core flooding with silica nanofluid after brine showed improve in oil recovery	McElfresh et al., 2012
Bismuth telluride (5.75 to 12.68) grams per gram of water	-	2.5-10.4	Glass substrates Silicon wafer substrates	De-ionizer water	Contact angle	-Addition of nanoparticles increased contact angle -Smaller nanoparticles size led to larger change in contact angle -Contact angle increased when concentration is increased until reaching a maximum and then started decreasing	Vafaei et al., 2006

7. Wettability alteration at high temperature

Thermal operations improve oil recovery by different mechanisms such as viscosity and IFT reduction, thermal expansion and wettability alteration. Distinguishing the contribution of each mechanism has been controversial issues in the literature. Different opinions in literature regarding the influence of high temperature on the wettability of sandstone and carbonate were documented by Rao (1999). Using contact angle measurements, he showed that sandstone may acquire oil-wet or water-wet state at high temperature while carbonate becomes more water-wet when the temperature is increased.

Silica surfaces generally alter to be oil-wet in high temperature. However, the opposite effect was also observed. High temperature may induce calcium carbonate precipitation from reservoir brine on the silica surface. When covered by calcium carbonate silica surface becomes water-wet Rao (1999). He concluded that many factors control how high temperature influences the wettability of sandstone including brine composition and pH.

Schembre et al. (2006) found that sandstone become more water-wet at high temperatures. This was attributed to fine detachment from rock surface at elevated temperature (Schembre et al., 2006). They also mentioned that water film on pore surfaces became more stable at high temperature. Tang and Morrow (1999) referred to crude oil brine rock (COBR) as the possible mechanism of wettability alteration and not only rock/brine interaction. The range of the temperature that was tested was up to 230°C.

Babadagli (1996) carried out capillary imbibition tests on Berea sandstones at different temperatures. The results indicate that increasing temperature from 27.5°C to 80°C enhanced the imbibition rate and final recovery. Decrease in oil viscosity and IFT at elevated temperature contributed to improved oil recovery. He indicated that higher imbibition rate at higher temperature is mainly due to viscosity reduction and the effect of wettability alteration and IFT reduction on the improved recovery was minimally low.

Gupta and Mohanty (2010b) conducted imbibition tests using several anionic and nonionic surfactants under different temperatures up to 90°C. They found that high temperature increased the ability of surfactants to imbibe spontaneously into limestone samples. Improvement of spontaneous imbibition is attributed to the gravity forces that were enhanced by viscosity reduction. Al-Hadhrami and Blunt (2001) conducted an analytical study based on an experimental research. The data used shows that spontaneous imbibition of water at elevated temperatures (around 240°C), enhanced leading to about 27 to 35 % OOIP incremental oil recovery. As no imbibition occurred at the reservoir temperature, they attributed this improvement to wettability alteration at elevated temperatures. Based on this data, a 1 D model for imbibition and heat transport in the rock matrix was developed. The model predicted that approximately 30% OOIP could be achieved in a single matrix after 700 days of steam or hot water flooding in comparison with only 2% production under natural aquifer drive.

Hamouda and Gomari (2006) conducted a wettability alteration study on carbonate reservoirs using contact angle, IFT, and Zeta potential measurements to account for the effect of temperature. They found that changes in contact angle at high temperatures followed the same trend as the changes of IFT. The contact angle reduced from 160° to 68° at high temperatures, indicating that wettability of carbonate is reversed from oil-wet to water-wet when temperature is increased. As temperature increased, the positive charge on the calcite surface was reduced, which in turn increased the repulsive forces between the calcite surface and the adsorbed organic components. They concluded that there is a critical temperature for maximum possible wettability alteration that can be attained. If the temperature increases above this value, no further wettability alteration can be achieved (Hamouda and Gomari, 2006). A summary of selected published studies on wettability alteration nanofluid is given in **Table 5**.

Table 5: Selection of published studies on wettability alteration at high temperature

Temperature	Material	Brine	Range of recovery	Tests	Results	Reference
45 to 230°C	Diatomite (sandstone) plugs	Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , Cl ⁻ , HCO ₃ ⁻	~32%	Contact angle Imbibition test	-Light oil (34API) -Contact angle reduced from 18.3° at 45°C to 0° at 230°C -Reduction of oil to water viscosity ratio at high temperature results in less resistance to water imbibition and also change the wettability to be more water-wet	Schembre et al., 2006
25 to 130°C	Calcite crystals Chalk plugs(carbonate)	Distilled water	~11%	Contact angle Zeta potential Imbibition test	-Model oil and Heptane -Contact angle decreased from 160° at 25°C to 68° at 130°C -Zeta potential reduced from 2.95 mV at 20°C to 0.45 mV at 50°C	Hamouda and Gomari, 2006

8. Potential wettability modifiers

8.1- Microbial method. Although its effects on the reduction of IFT are well known, microbial enhanced oil recovery was suggested as a new method for wettability alteration. A study by Kowalewski et al. (2006) documented the results of microbial enhanced oil recovery in sandstones. They reported that bacteria may reduce the residual oil saturation by two mechanisms: (1) IFT reduction and (2) wettability alteration. When bacteria were allowed to grow on sandstone surfaces, the IFT is reduced significantly. They also suggested that more IFT reduction can be achieved when bacterial growth increased. Sandstone cores used during the study was strongly wet-wet and the Amott indices showed no change in the wetting state. The authors, however,

stated that dynamic of imbibition by microbial may indicate an alteration of wettability towards less water-wet state. The behaviours of microbial enhanced oil recovery in some core samples were not identical and the authors attributed this difference to bacterial growth rate. They conclude that wettability alteration by microbial methods is controlled by the initial state of the wettability. If the initial wetting state is water-wet, it may become less water-wet and if it is oil-wet it shifts to be more water-wet.

A study on the effect of *E. cloacae* strain bacteria on the wettability was reported by Karimi et al. (2012b). Both contact angle and AFM was used to investigate the ability of *E. cloacae* to change the wettability of oil-wet silica surfaces. This bacterium was observed to change the wettability of aged microscope glass slides toward more water-wet. Bacteria were believed to adsorb on the silica surface removing the organic layer that rendered the surface oil-wet. Water contact angle was reduced from 115° to 8.7° after 2 days of bacterial solution exposure when mineral salt solution was used. The wettability consequently changed from oil-wet to water-wet (Karimi et al., 2012b).

The above discussion indicates that bacteria may have different effects on wettability depending on their composition. In fact, a similar observation was reported by Afrapoli et al. (2009). They tested the spontaneous imbibition of two growth variants of alkane oxidizing bacterium, *Rhodococcus* sp. 094. Surfactant producing bacteria solution was observed to reduce the water-wetting of silica, while non-surfactant-producing bacteria were able to alter the wettability to be more water-wet. Further investigations on the mechanism of wettability alteration by microbial methods are needed to clarify these controversial effects.

8.2- Ionic liquids. Ionic liquids are new type of chemicals that have been recently studied extensively for different fields of applications. These applications include thermo-electrochemical cells (Armand et al., 2009), CO₂ capture (José-Alberto et al., 2011), catalyzed reaction (Dyson and Geldbach, 2007), and even as a green solvent (Rogers and Seddon, 2003). Ionic liquids are defined as salts that have low melting temperature (Wasserscheid and Keim, 2000) and therefore, can be found in liquid state at ambient conditions. They are environmentally friendly and considered green solvents (Rogers and Seddon, 2003). Their low vapor pressure and strong dissolving characteristics make them safer and more efficient in compare with other organic solvents.

There are a few publications on the application of ionic liquids in oil refining process. Lo et al. (2003) and José-Alberto et al. (2011) reported that ionic liquids can be used to extract and oxidize sulfur compound in light oil. Hu and Guo (2005) found that ionic liquids can be efficiently

employed to reduce asphaltene precipitation. José-Alberto et al. (2011) provided a detailed list of the possible applications of ionic liquids during CO₂ injection to reduce asphaltene deposition in the reservoir.

Joonaki et al. (2012) investigated the effect of several ionic liquids in heavy oil using spontaneous imbibition and core flooding tests. They concluded that ionic liquid that have hexafluorophosphate anion [PF₆]⁻ and tetrafluoroborate anion [BF₄]⁻ will produce Hydrogen fluoride HF gas when they are mixed with heavy oil. They tested a new ionic liquid on heavy oil sample. Free imbibition tests showed that recovery factor improved from 41% to 74% when the new ionic liquid was mixed with heavy oil. The new prepared ionic liquid was reported to upgrade heavy oil by reducing asphaltene content, viscosity, and, average molecular weight of heavy oil.

Recently, several studies investigated the use of ionic liquids in oilsands extraction. Painter et al. (2009), Williams et al. (2010), and Painter et al. (2010) studied the ability of different ionic liquids to separate bitumen from oil sand. They reported that about 95% of oil can be recovered using ionic liquid extraction. After oil extraction, ionic liquid can be separated and recycled several times. They also showed that some of ionic liquids were inefficient because they agglomerated after interaction with oil sand. Ionic liquids that worked efficiently were 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate, BMMIM BF₄ and 1-ethyl-3-methylimidazolium tetrafluoroborate EMIM BF₄ (Painter et al., 2010; Li et al., 2011).

In attempt to explore the potential of using ionic liquid in enhanced oil recovery, Benzagouta et al. (2013) screened different ionic liquids established from AmmoengTM group by measuring their IFT with crude oil. They found that ionic liquid Ammoeng 2 was able to reduce IFT with crude oil better than surfactant Triton X-100. Upon mixing Ammoeng and Triton X- 100, they showed that the IFT values were a function of different factors such as total concentration and the surfactant to ionic liquid mass ratio. Temperature was also found to be critical on IFT reduction by ionic liquids. A more recent screening study by Dahbag (2014) also listed Ammoeng 2 to be optimum option. The study screened ammonium and phosphonium ionic liquids based on their solubility in water, thermal stability and IFT trend with temperature. Ionic liquid Ammoeng 2 was observed to be stable at temperatures as high as 80°C.

Mohammed and Babadagli (2013) used ionic liquid for wettability alteration by dissolving different ionic liquid in water. An ionic liquid solution was able to recover diluted oil (heavy oil mixed with solvent) from oil-wet carbonate surface after the cores were exposed to pre solvent phase.

Enhanced oil recovery by ionic liquid can be explained based on its effect on IFT and the adhesion force. Malham et al. (2006) and Liu et al. (2006b) measured the IFT of ionic liquid-water mixtures at different liquid concentrations. Only a dilute amount of ionic liquid (~0.03 % mass fraction) was required to decrease IFT of the mixture from 73 millinewtons per meter mN m^{-1} to its minimum value at 40 mN m^{-1} . It is observed that the adhesion energy between bitumen and Alberta oil sand was reduced to $0.4 \text{ millijoules per millimeter mJ/m}^2$ compared to 4 mJ/m^2 in KCl solution (Hoshead et al., 2010). Ionic liquid offers a great potential as a wettability alteration agent as it affects both rock and fluid properties and because it can be customized to serve specific application.

9. Opportunities and challenges

To induce wettability alteration, i.e., make the system more water-wet, a chemical or thermal treatment must be applied. Several chemical and thermal methods were suggested in literature and each of these methods has certain limitations and challenges that should be carefully considered. Depending on conditions of the candidate reservoir and the availability of wettability alteration agents, some of the chemical and thermal methods may be more attractive than others. For example, using low salinity water would be more appealing if a fresh water source is available nearby. The use of some chemicals may be regulated by environmental legislations. Thermally induced wettability alteration in deep reservoirs is a challenge as steam loses its quality as it travels deeper into the reservoir and very high temperatures are needed for this process. The opportunities and challenges of each of the previously introduced wettability modifier are presented in this section.

9.1- Surfactant. There is a wide range of surfactant that can be selected for wettability alteration. Surfactants can also be mixed to create a new surfactant blend with different properties. Similar to other EOR processes, using surfactants wettability alteration has always faced the limitation of surfactant cost, which is a function on the surfactant concentration. The concentration that is required for wettability alteration by surfactant in carbonates does not usually exceed the CMC concentrations. For example, Standes and Austad (2000) found that there is no significant difference in oil recovery by spontaneous imbibition when the concentration of cationic surfactant was increased from 1.0 wt.% to 5 wt.%. They concluded that wettability alteration by cationic surfactants is optimized at a concentration around or slightly higher than CMC. The application of alkaline anionic surfactant requires only dilute amount of anionic surfactant. Hirasaki and Zhang (2004) used about 0.05 wt. % of anionic surfactant CS-330 to successfully alter the wettability of carbonate. The search for cheaper surfactant for wettability alteration is ongoing. For example,

Standes and Austad (2000) found that a low cost ammonium surfactant, which is commercially available surfactant, contains the similar effective materials cationic surfactant C12TAB.

Surfactant adsorption on the rock surfaces is one of the major reasons that cause surfactant loss. Many studies have investigated reducing the surfactant adsorption to minimize the overall cost of surfactant consumption. Surfactant adsorption usually increases as surfactant concentration increases and reaches a maximum at critical micelle concentration (CMC). Obviously, reducing the surfactant concentration effectively minimizes the adsorption as well as the cost of surfactant. Another way to reduce the adsorption is to use alkaline with surfactants. Na_2CO_3 can reduce the adsorption of anionic surfactant at low concentrations. Wettability alteration by surfactant is limited by the ability of surfactant diffusion and adsorption onto the rock surface. Stoll et al. (2008) showed that a diffusion of surfactant represent a serious challenge when wettability alteration by surfactant is upscaled. Surfactant diffusion can be enhanced by viscous forces (Wang et al., 2011) or by increasing the temperature (Standes and Austad, 2000).

Many types of surfactants were suggested in literature. Surfactant screening study should be performed to select the optimum surfactant system. Stability of surfactant at high temperature is one of the limitations of using surfactant in wettability alteration for high temperature high pressure reservoirs. Dual surfactant was used successfully to increase thermal stability of surfactant. Sharma et al. (2011), for example, combined cationic surfactant and nonionic surfactant to create thermally stable surfactant solution at temperatures higher than 100°C . Each of the combined surfactants was not stable at 100°C .

9.2- High pH solutions. As explained in Section 6, high pH solutions can be used be effectively in wettability alteration in sandstone and limestone. Alkali consumption on rock surface could hinder efficiency of wettability alteration process. Alkalis found to be consumed on anhydrite more than other minerals. Interactions of alkali with rock minerals can lead to permeability reduction due to secondary precipitation of minerals. Another limitation that could negate the alkali effect is pH buffering. Fortunately, there are several alkalis that have relatively low consumption on the rock surface. For example, NaBO_2 is less consumed the anhydrite than Na_2CO_3 . One of the other issues that could arise during alkali flooding is the increased sulfate concentration when Na_2CO_3 are used as alkalis (Kazempour et al. 2011).

9.3- Nanofluids. Many studies tested the efficiency of combining two or more wettability modifiers. When two wettability modifiers are combined, one of them will be the primary wettability alteration agent. A secondary wettability modifier may be used to enhance the efficiency of wettability adjustment process. For example, nanofluids are usually combined with

different types of surfactants. In a study by Giraldo et al. (2013), anionic surfactants were used as a primary wettability modifiers and alumina was observed to increase the adsorption of surfactant in oil-wet sandstone and thus enhances its ability to alter the wettability of sandstone. In other cases, nanofluids are used as a primary wettability alteration agent. Karimi et al. (2012) used zirconium nanofluid to change the wettability of oil-wet carbonate cores. A combination of non-anionic surfactants was used to stabilize the suspension of zirconium nanofluid.

Other methods were also used to stabilize the colloidal dispersion of nanoparticles such as modification of particles surfaces or the pH of the solution. Consequently, the need for surfactant is eliminated. For instance, Maghzi et al. (2012) employed silica nanoparticles to modify the wettability of oil-wet micro glass only by using water as a suspending fluid. The wettability of silica nanoparticles was modified to be lipophobic hydrophilic. Acquiring stable nanofluids without surfactants is desired to decrease the overall cost of the process.

Note that although many experimental studies show that nanofluids can reduce IFT and contact angle, this might not be reflected as an improved oil recovery method. Also, similar to surfactants, nanofluids are more efficient in light oil than in heavy oil (Roustaei et al., 2010).

The limitations of using nanofluid as wettability modifiers are directly related to their tendency to be unstable in the long-term leading to nanoparticles agglomeration and precipitation on the rock surfaces. Different methods for nanofluid stability are given in Section 6. Generally, stability of nanoparticles colloidal suspension can be enhanced by increasing repulsive forces between the nanoparticles over the attraction forces. The direct impact of the particles precipitation process is to lose the unique properties of the nano-suspension and the inability to distribute the particles homogeneously in different parts of the reservoir.

The stability of nanofluids is functions of the type, size, and concentration of the nanoparticles in the dispersion. It has been demonstrated that if concentration is increased beyond certain limit, particles may agglomerate and form clusters and this consequently leads to porosity/permeability impairment. Therefore, selection of the optimum nanoparticles type, size, and concentration in addition to proper stabilization method are immensely vital factor for the application of nanofluid in wettability alteration.

9.4- Thermal methods. Using hot water/steam as a wettability modifier in sandstone and carbonate reservoir was tested by many studies. Rock mineralogy oil composition appears to have a direct impact on whether sandstone becomes more oil-wet or water-wet. In carbonate reservoir,

however, temperature seems to adjust the wettability only toward more water-wetness. For example, Motealleh et al. (2005) observed that hot water (225°C) resulted in spontaneous imbibition of water into tubes filled with oil-wet carbonate samples. Note that applying such high temperatures in the field may be faced with many practical, economic, and environmental concerns. For heavy oil, however, this option may be more attractive than chemical methods. There is no field scale proof of wettability alteration at elevated temperatures.

Chemically induced wettability alteration can be enhanced at high temperatures. Standes and Austad (2000) showed that the imbibition rate of surfactant solution into oil-wet carbonate core at 70°C was twice that of at 40°C.

9.5- Smart water and low salinity water. The chemical composition, salinity, and pH of the injected water play a significant role in changing the surface properties of the rock and thereby, the wettability of an oil-wet porous medium. Wettability alteration of oil-wet sandstone by low salinity water has been extensively studied by many researchers. In addition to satisfying some conditions to be applied successfully (Buckly and Morrow, 2011), another important factor to be considered is the availability of fresh water sources nearby. High salinity water that contains multi divalent ions, on the other hand, is able to change the wettability of oil-wet carbonate reservoir as explained in Section 6. One of the major limitations of using high salinity water it is not efficient in low temperature. A high temperature medium is needed to speed the reaction of multi-divalent ions.

10. Wettability alteration in heavy-oil containing oil-wet fractured reservoirs

Few attempts have been made to investigate the wettability alteration in the heavy-oil containing oil-wet fractured reservoirs. In such complicated systems not only the rock characteristics should be altered (wettability), the crude oil properties must also be changed. Therefore, solvent-based processes can be indispensable for recovering heavy-oil from oil-wet fractured reservoirs. When solvent is injected, it diffuses into the matrix system and reduces both density and viscosity of heavy-oil which will then be produced containing fraction of the injected solvent. At the end of the process, a considerable amount of diluted oil (original heavy oil the mixed with injected solvent) remain in the oil-wet matrix system. Provided that wettability of the matrix is altered from oil-wet to water-wet, diluted oil can be drained by water imbibition improving both oil-recovery and solvent retrieval.

Mohammed and Babadagli (2014a) tested this hypothesis using recovery process that is composed of two phases: (1) Solvent phase and (2) wettability alteration phase. Two types of rock were used to represent different state of wettability. Limestone cores were used as strongly oil-wet systems while aged Berea sandstone cores were considered weakly water-wet systems. A heavy crude oil of 3600 cp viscosity was used to saturate both types of rocks under vacuum at 65°C. After one week of saturation, limestone cores became strongly oil-wet while Berea sandstone cores were water-wet as indicated by contact angle measurements. Sandstone cores were aged under the same saturation conditions for 6 weeks before acquiring a weakly water-state. Solvent phase was applied using two types of solvent: heptane and diluent oil.

Mohammed and Babadagli (2014b) compared oil recovery during wettability alteration phase for two cases. For the first case, sandstone and limestone core samples saturated with heavy oil were placed directly into imbibition cells filled with wettability alteration chemicals (anionic surfactant for sandstone and cationic surfactant for limestone). Only 8% of oil was recovered from the sandstone core. The recovery for limestone was as low as 2%. In the second set of experiments sandstone and limestone core samples that was saturated with the same heavy crude oil (3600 cp) was immersed in heptane for 10 days and then put directly in imbibition cell that was filled with the same wettability alteration chemical that was used in the first set of experiments. Diluted oil recovery increased dramatically from about 8% to 57% for sandstone while it reached 40% for limestone up from 2% (**Figure 5**). These results show the importance of the solvent phase for the subsequent wettability alteration phase.

This was also confirmed by using another solvent, which has a higher mixing capability. Mohammed and Babadagli (2014b) reported that diluent oil recovery for sandstone was increased from 57% to 63% when the diluent oil was used in solvent phase instead of heptane. It is obvious that a higher efficiency of water imbibition during wettability alteration is directly related to the extent of dilution that can be achieved by solvent. This indicates that both solvent type and soaking period should be optimized to increase the efficiency of the process. Another important factor is the type of wettability alteration agent. Based on the discussion provided in previous section, there are list of chemicals that have higher ability to alter the wettability in sandstone than limestone and vice versa. Screening of wide range of chemicals by Mohammed and Babadagli (2014b) revealed a group of chemicals could potentially alter the wettability of sandstone and limestone toward water-wetness. Short listed chemicals are provided in **Table 6**.

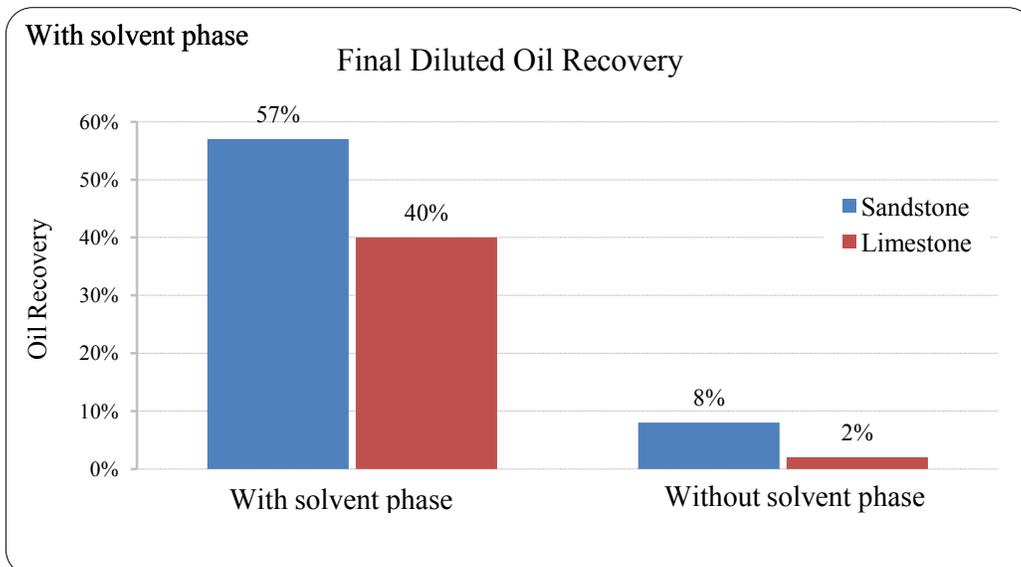


Figure 5: Diluted oil recovery during wettability alteration phase for cases with and without solvent phase.

Table 6: Chemical used for wettability alteration tested by Mohammed and Babadagli (2014b).

Sandstone	Limestone
Anionic surfactant CS-330 (1 mmole/l)	Cationic surfactant C12TAB (1 wt.%)
Anionic surfactant Alfoterra -8S (Alf-8S) (1 mmole/l)	Anionic surfactant CS330 (1 mmole/l)
Distilled water	Distilled water
NaBO ₂ (2.5 wt.%)	NaBO ₂ (2.5 wt.%)
Ionic Liquid BMMIM BF ₄ (1 wt.%)	Ionic Liquid BMMIM BF ₄ (1 wt.%)
Alumina nanoparticles (1 wt.%)	Zirconium nanoparticles (1 wt.%)

Sandstone case

Figure 6 shows the wettability alteration indicated by final diluted oil recovery for selected experiments from Mohammed and Babadagli (2014b). It can be seen that distilled water was able to produce about 52%. It was discussed in section 6 that lowering the salinity of injected water increases the repulsive forces between rock sandstone surface and the adsorbed organic components. A recent study by Morsy and Sheng (2014) performed on shale core samples showed that distilled water improved oil recovery in shale core samples almost double 2% KCl brine. They attributed the efficiency of distilled water to the clay swelling effect.

Oil recovery by ethoxylated sulfate anionic surfactant STEOL™ CS-330 (3 ethylated groups) was increased to 59%. Salehi et al. (2008) showed that anionic surfactants can desorb the cationic organic components from sandstone surface and thus adjust the wettability to be more oil-wet. Propoxylated sulfate anionic surfactant Alfoterra™ 145-8S (8 propoxylated group) was not efficient as CS-330 with a final recovery of 30%. Ionic liquid BMMIM BF₄ was able to increase diluted oil recovery to more than 63% better than all other chemicals that were tested. As explained in section 6, ionic liquid can affect both rock characteristics and fluid properties. Mohammed and Babadagli (2014) attributed the efficiency of ionic liquid to its ability to reduce the IFT and adhesive forces. Alumina nanofluid was reported by Giraldo et al. 2013 to have the ability to enhance the wettability alteration induced by surfactant solution. About 25% diluted oil recovery was obtained when alumina nanofluid was used in aged sandstone core. No surfactant was added to the system.

High pH solution with NaBO₂ resulted in a relatively slow but eventually resulted in the second highest oil recovery. The 60% of diluted oil that was recovered by NaBO₂ shows that increasing the pH of injected water may reduce the attraction forces between silica and organic materials that caused the oil-wetness of rock surface.

Limestone case

Overall, it appears that diluted oil recoveries in limestone were less than those with the sandstone samples which can be attributed to the strong oil-wetness characteristics of the limestone (**Figure 7**). Cationic surfactant C12TAB, on the other hand, imbibed spontaneously into limestone displacing about 40% of the diluted oil. As stated in Section 6, Standes and Austad (2000) observed that cationic surfactant type CnTAB can alter the wettability of chalk which saturated with light oil (crude oil: heptane 60:40 by volume). Obviously similar conclusion can be made on heavy oil if a solvent phase is applied. While anionic surfactants cannot alter the wettability of limestone by ion pair interaction, they can still improve oil recovery in by reducing IFT (Standes and Austad, 2000). About 30% of diluted oil was recovered using ethoxylated sulfate anionic surfactant STEOL™ CS-330.

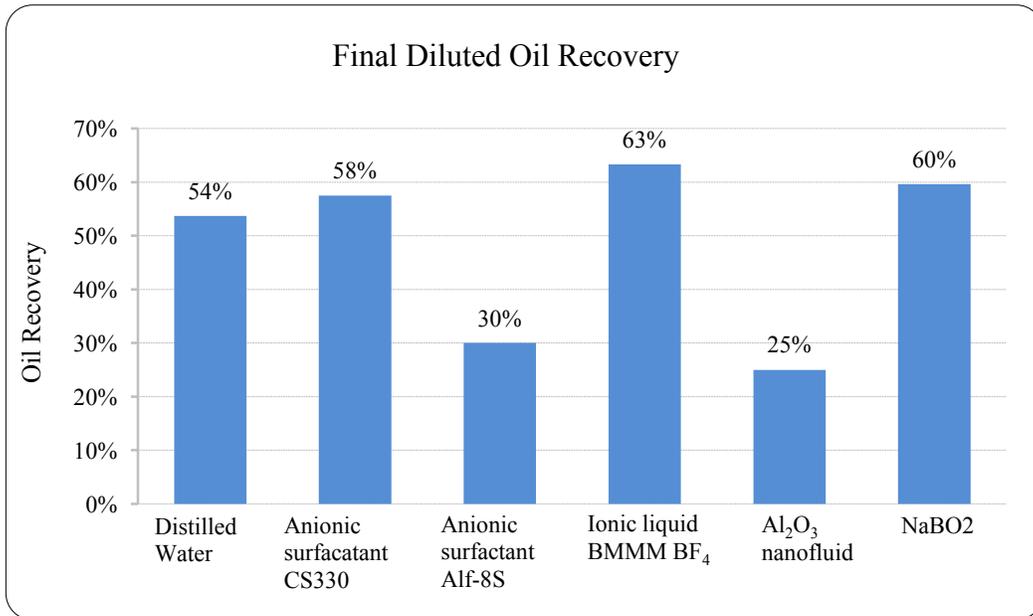


Figure 6: Diluted oil recovery during wettability alteration phase for sandstone cores (reproduced after Mohammed and Babadagli, 2014b).

Zirconium nanoparticles dispersed in water was tested as wettability modifier in light oil systems by Karimi et al. (2012). Mixture of non-ionic surfactants was used as suspending fluid. Mohammed and Babadagli (2014B) used water as a suspending fluid. As shown in **Figure 7**, zirconium nanofluid was able to recover an amount of diluted oil is similar to anionic surfactant. Ionic liquid BMMIM BF₄ resulted in the best diluted oil recovery as was the case in sandstone, which indicates that can adjust the wettability of both silica and carbonate to be more water-wet. No conclusive explanation of the mechanisms of wettability alteration by ionic liquids was provided by Mohammed and Babadagli (2014b). However, this study shows that both reduction of IFT and adhesive force might contribute to the improved oil recovery.

Similar high pH brine that was used to alter the wettability of sandstone was tested on limestone by Mohammed and Babadagli (2014b). They referred to a study by Zhang et al. (2008), which pointed out the efficiency of NaBO₂ to alter the wettability of carbonate better than other alkalis. Figure 6 indicates that NaBO₂ was able to alter wettability in the limestone cores as strongly as the cationic surfactant C12TAB. It was explained in section 6 that reducing pH of oil-wet system is believed to decrease positive charges of carbonate rock surfaces and hence increase the repulsion force between the surface and organic adsorbed matter. Wettability will be then altered to be more water-wet.

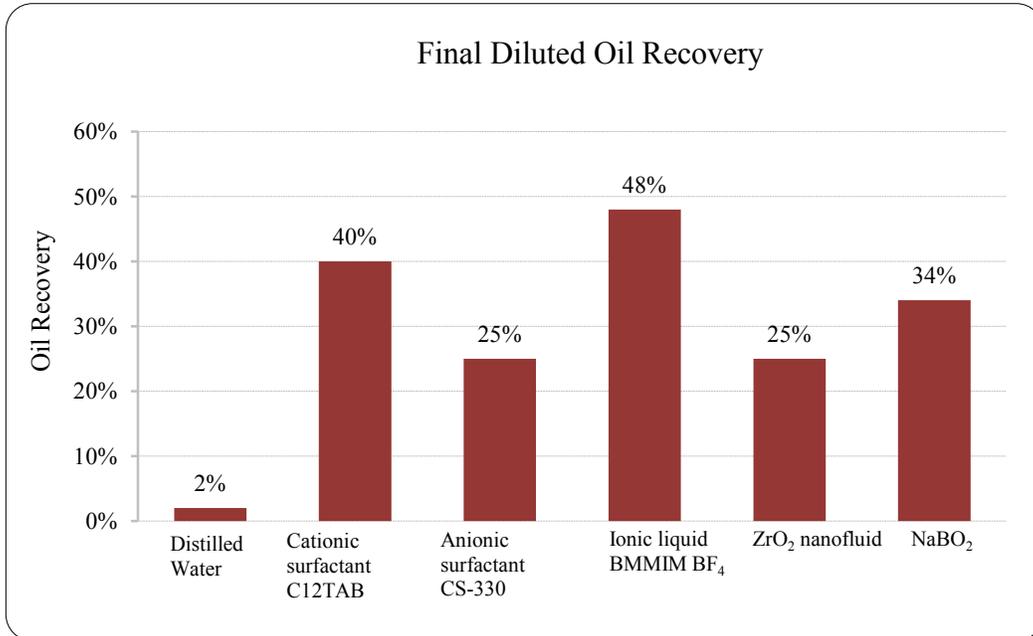


Figure 7: Diluted oil recovery during wettability alteration phase for limestone cores (reproduced after Mohammed and Babadagli 2014b)

Grosmont carbonate samples

The challenge of recovery bitumen (5-9 °API-1,600,000cp) from Grosmont carbonate was studied by Mohammed and Babadagli (2014b). A preserved core was immersed in heptane for 3 weeks and then put into water for one week. Oil recovery during this period was negligible, which confirmed the oil-wetness of the Grosmont core. Water was then exchanged with alkaline NaBO₂ solution (2.5 wt.%). Oil displacement started immediately indicating that wettability of Grosmont was altered to more water-wet. Changing the pH of the injected water using NaBO₂ was shown to significantly affect the electrostatic forces between carbonate surfaces and adsorbed organic matters. It was concluded that a combination of solvent phase can efficiently improve oil recovery in heavy-oil/bitumen containing oil-wet fractured carbonate reservoirs (Mohammed and Babadagli, 2014b).

11. Conclusions and remarks

Wettability is one of the most critical characteristics of rock-fluid systems in oil recovery. Its alteration to more favourable water-wetness efficiently is a critical problem. A systematic approach for a wettability alteration processes was provided in this paper. The following are the highlights from this extensive review.

1. Wettability alteration process in each reservoir is a unique process and requires the understanding of the mechanisms that caused a reservoir to be oil-wet.

2. Chemical induced wettability alteration is suitable in light oil reservoirs while thermal methods are more attractive in heavy oil reservoirs. To apply chemical wettability alteration in heavy oil reservoirs, oil properties has to be changed thermally or using solvents.
3. Although contact angle measurement gives a fast and economical mean to evaluate the alteration of surface wettability, the results might be misleading; therefore, it should be integrated with another measurement tool.
4. Spontaneous imbibition test is the most reliable tool for wettability alteration measurement. The shape of imbibition curve, ultimate oil recovery and the visualization of the oil production from different core faces provide valuable information to analyze the mechanisms of wettability alteration.
5. Wettability alteration may increase oil recovery by gravity or capillary imbibition.
6. Surfactants are the most studied wettability modifier in literature. Yet, there is no agreement on screening criteria to determine which type of surfactant is best for carbonate or sandstone. It is difficult to describe a general type of surfactant (i.e., anionic, cationic, or non-ionic) as a better wettability modifier than the other type. An efficient wettability modifier for certain type of rock can be found in any of these surfactant groups.
7. Ammonium surfactants are the most cited successful wettability modifier for carbonates, while ethoxylated surfactants are the most cited successful wettability alteration agent in sandstones.
8. High pH solutions represent one of the most feasible wettability modifiers .They can alter the wettability of sandstone and carbonate. Alkaline may be injected with surfactant to enhance the wettability alteration at optimum salinity. The type and the concentration of alkaline should be carefully selected to minimize the consumption of alkaline on the rock surfaces`
9. Low salinity water may adjust the wettability of oil-wet sandstone to be more water-wet while high salinity water that contains optimum composition of divalent ions shift the wettability of oil-wet carbonate toward water-wet. However, wettability alteration by multi divalent ions is dependent on temperature to a great extent.
10. Zirconium and modified silica nanofluid are able to shift the wettability of carbonate toward water-wetness, alumina nanoparticles change wettability of oil-wet sandstone. It should be noted, however, that nanofluid can impose adverse effects on the reservoir properties such as permeability damage.
11. Microbial enhanced oil recovery and ionic liquid may provide potential opportunity to be used as wettability modifiers.
12. Experimental studies on wettability alteration in heavy oil containing oil-wet systems are rare. Direct injection of chemical solutions to alter the wettability in this type of reservoir may not be feasible without prior treatment for fluid properties.
13. Solvent injection followed by wettability modifiers injection was applied successfully to

recover oil recovery in oil-wet systems that contain heavy oil/bitumen. Cationic surfactant type C12TAB, high pH solution using NaBO₂, ionic liquid of BMMIM BF₄, and zirconium nanoparticles can alter the wettability of heavy oil containing oil-wet carbonate reservoirs while anionic surfactants CS-330, high pH solution NaBO₂, ionic liquid BMMIM BF₄, and alumina nanofluid can alter the wettability of oil-wet sandstone (by aging them) reservoirs when they are injected after solvent treatment.

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CHAPTER 4: ALTERATION OF MATRIX WETTABILITY DURING ALTERNATE INJECTION OF HOT- WATER/SOLVENT INTO HEAVY-OIL CONTAINING FRACTURED RESERVOIRS

This paper is a modified and improved version of SPE 170034, which was presented at the SPE Conference held in Calgary, Alberta, Canada, 10–12 June 2014. A version of this chapter has been submitted to SPE Reservoir Evaluation & Engineering for publication.

Preface

An alternate injection of solvent and hot water/steam called Steam-Over-Solvent injection in Fracture Reservoirs (SOS-FR) has been recently suggested and tested by our research group. In this process, most oil is produced during the solvent phase and then hot water/steam phase is assigned, mainly to retrieve the solvent. Oil recovery during this phase is typically low due to limited thermal expansion in the case of oil-wet matrix, and because capillary imbibition and gravity drainage driven by viscosity reduction do not have a significant contribution to the recovery. Wettability alteration toward more water-wet state will, however, enhance these mechanisms.

Based on these facts, different wettability alteration agents were tested including cationic and anionic surfactants, ionic liquids, nano-fluids, high pH solutions, and low salinity water. The potential of these materials to modify the wettability of aged sandstone and limestone samples was evaluated using imbibition tests.

Berea sandstone (aged to be oil-wet) and Indiana limestone samples were saturated with heavy oil (3,600 cp). After the wettability modification was confirmed using different tests, the SOS-FR method was applied. The process was initiated by soaking cores into solvent (heptane or diluent oil) and the oil recovery was estimated using refractive index measurements. Then, two different experimental schemes were followed. In this first scheme, different chemicals were used and the oil production readings were taken periodically. These experiments would yield additional oil recovery (and solvent retrieval) by capillary imbibition and enhance gravity drainage if the wettability alteration was achieved. In the second scheme, the solvent-heptane was retrieved first by hot-water exposure and the capillary imbibition tests were performed to test the selected chemical additive solutions as the wettability alteration agents.

After conducting a total of 35 experiments, the most promising wettability alteration agents were marked and optimal application conditions (i.e., temperatures, injection sequence) were identified.

1. Introduction

The poor response of naturally fractured and oil-wet reservoirs (NFOWR) to water-based enhanced oil recovery methods leads eventually to inefficient oil recovery. If these reservoirs contain heavy crude oil, the oil recovery process is further complicated. One of the suggested solutions for heavy-oil recovery from this type of reservoir is solvent injection (Hatiboglu and Babadagli 2008). However, this requires special design to maximize not only the recovery but

also solvent retrieval. Al-Bahlani and Babadagli (2008) proposed a scheme to achieve this and introduced a method called “Steam-Over-Solvent Injection in Fractured Reservoirs” (SOS-FR). One of the advantages of this method is the ability to retrieve a great amount of the injected solvent through low temperature steam (even hot water) injection. This retrieval process is based on boiling of solvent. In other words, solvent retrieval relies on the expansion of solvent also carrying out additional oil and is purely a thermodynamic process. If one is able to change physiochemical properties of the matrix of the NFORs, additional oil can be recovered with additional solvent retrieval at the end of the process. This can be achieved by wettability alteration so as to enhance capillary imbibition of injected water (or hot-water) at the end of the solvent injection process during SOS-FR method.

Alteration of matrix wettability in NFOR is a challenge even in light oil systems. In case of heavy-oil containing reservoirs, oil needs to be diluted by heating or solvent first. Then, water (or hot-water) containing wettability alteration agents are injected. This paper reports the results of wettability alteration process using different wettability alteration chemicals and processes. Firstly, potential wettability alteration chemical solutions that can be used during the alternate injection of hot water and solvent (SOS-FR methods) were tested. Secondly, the effect of solvent dilution-retrieval process on the wettability of oil-wet sandstone and limestone was clarified. Among the wettability modifiers tested in this study were chemicals known for their surface modification properties such as anionic, cationic surfactants, high pH solutions, as well as recently introduced chemicals such as nanofluids and ionic liquids.

2. Experimental Setup and Methodology

Outcrop Berea sandstone (average porosity: 20%, permeability: 300-500 md) and Indiana limestone (average porosity: 20%, permeability: 10-40md) core samples were saturated with a heavy crude oil (3,600 cp) obtained from a field in Alberta, Canada. Properties of rock samples and heavy oil are shown in **Tables 1 and 2**. Berea sandstone cores were aged in the crude oil under vacuum for six weeks at 65°C. The aging time of limestone was restricted to seven days. Contact angle measurements indicated that the wettability of sandstone cores was changed from strongly water-wet to weakly water-wet while limestone samples exhibited strongly oil-wet behavior. The pore volumes of core samples were calculated based on the weight difference of the cores before and after saturation.

Three phases were applied during the experiments: (1) Solvent dilution phase, (2) wettability alteration phase, and (3) solvent retrieval phase. Different case scenarios were applied to test the efficiency of each phase and test how each interacted with other phases. In some experiments, one

or two of the mentioned phases were skipped as will be explained later. This will also determine the most appropriate way to apply this modified version of the SOS-FR method with an inclusion of wettability alteration.

To mimic matrix-fracture interaction of a natural fractured system, all three phases were performed in imbibition cells where the gap between core samples and imbibition glass represented the fracture portion. Wettability alteration phases were applied by placing the cores immediately into same size imbibition cells that were filled with a selected wettability modifier to avoid any loss of solvent. Oil recovery during this phase was observed by monitoring the amount of oil produced at the upper part of imbibition cell.

During the solvent phase, the cores were soaked into heptane or diluent oil for 10 days. Oil recovery during this phase was estimated using refractive index measurements, weight differences, and volumetric calculations. Then, the cores were immediately immersed into imbibition cells containing different wettability alteration solutions. A selection of twelve chemical solutions was used in the wettability alteration phase. **Table 3** displays the properties of the chemicals used in wettability alteration. Most of the experiments in this phase were conducted at room temperature. Only a few experiments were selected to be performed at 65°C to test the effect of temperature on the process. Solvent retrieval phase was conducted using the experimental setup shown in **Figure 1**. The oil recovery during the wettability alteration phase was given as a percentage of the pore volume that contained crude oil diluted with solvent.

3. Description of Experiments

3.1 Sandstone experiments. Fifteen experiments were run using sandstone core samples. All cores were aged in heavy crude oil for six weeks except core S8, which aged only for seven days to serve as water-wet core. Experiment S1 was used as a benchmark and no chemical solution was applied. Experiment S2 was carried out as a base case using anionic surfactant STEOL CS 330. Unless otherwise specified, STEOL CS 330 was used as wettability modifier during the wettability alteration phase. Experiment S3 was designed to test the repeatability of the results and was performed in a similar fashion to experiment S2. In both experiments, cores were first soaked into heptane for 10 days. Next, cores were put into imbibition cells filled with 1mmole/l surfactant STEOL CS330. This phase was run for 100 days. Solvent phase was skipped in experiment S4 to test the effect of solvent dilution on the process.

To investigate the effect of solvent type on the process, diluent oil was used as solvent in experiment S5. At the end of imbibition test, core S5 was exposed to a hot-water phase at 90°C to test the feasibility of adding a thermal phase at the end of wettability alteration process. Two

types of the ALFOTERRA® anionic surfactant group were used in experiment S6 and S7. The concentration of active component in both experiments was 1mmole/l. Experiment S8 was run with a water-wet core. In experiment S9, core was soaked into STEOL CS 330 for about 13 days and then was immersed into deionized water. The core sample in experiment S10 was immersed into water at 25°C for 16 days. The temperature was then increased to 65°C for 6 days. The objective of this experiment was to examine the effect of solvent retrieval on oil recovery.

In experiment S11, the core was immersed into an ionic liquid solution (50 wt.%). Experiment S12 was performed applying a different sequence. The wettability alteration phase for this core was applied after the solvent retrieval phase. Alumina oxide dispersion (500ppm) was used for experiment S13. The efficiency of high pH solutions on the wettability alteration of aged sandstone was tested in experiments S14 and S15. Chemical solution in experiment S14 was NaOH (2.5 wt.%). The core sample in experiment S15 was immersed into NaBO₂ (2.5 wt.%) solution.

3.2 Limestone experiments. All limestone cores were saturated with heavy crude oil for 7 days as previously described. Thirteen experiments were performed to represent different case scenarios. Similar to sandstone experiments, the benchmark experiment L1 was performed using water instead of chemical solution. Experiment L2 was the base case experiment for wettability alteration experiments and was run using cationic surfactant C12TAB (1 wt%). Note that C12TAB was used as chemical solution in the wettability alteration phase for limestone experiments unless otherwise stated. The core sample in experiment L3 was not exposed to solvent phase before the wettability alteration phase and immersed directly into C12TAB solution. Another type of cationic surfactants, ARQUAD 2C-75 (1 wt.%), was used in experiment L4.

Anionic surfactant 330 (1mmole/l) was used as a chemical solution in experiment L5. Alkaline anionic surfactant system was tested in experiment L6 using a solution of Na₂CO₃ (0.12 wt.%) and STEOL CS 330 (0.05 wt.%). In experiment L7, the core was first immersed into water for 13 days and then a brine with a composition of different divalent ions (Ca⁺², Mg⁺², SO₄⁻²) was used as a wettability modifier. The composition of the brine and the percentages of divalent ions are provided in **Table 4**. In experiment L8, the core was immersed into water at 25°C for 16 days and then temperature was increased to 65°C.

Imidazolium ionic liquid solution BMMIM BF₄ (1wt.% and 2 methyl group) was used in experiment L9. In core L10, the solvent was retrieved at 90°C before applying wettability alteration phase. Nanofluids were used in experiment L11, L12 and L13. In experiment L11, the

core was soaked into alumina oxide dispersion (500ppm) while zirconium oxide (1 wt.%) was tested for wettability alteration in experiment L12. Wettability alteration phase in experiment L13 was conducted using silica nanofluid (1 wt.%). To test the reproducibility of the data, experiment L14 was performed under the same conditions as experiment L2. Positive results were obtained using ionic liquid BMMIM BF₄ (1wt.%), therefore, four more experiments were carried out to investigate the efficiency of this chemical under low and higher concentrations. Concentrations in experiments L15, L16, L17, and L18 were 0.1, 0.5, 3.0, and 50 wt.%, respectively. The ionic liquid solution BMIM BF₄ (1wt %, 1 methyl group) was examined in experiment L19. High pH solution NaBO₂ (2.5 wt.%) was investigated in experiments L20.

4. Results and discussion

4.1 Diluted oil recovery, final oil recovery, non-solvent oil recovery and solvent retrieval.

Several terms were used in this study to describe the amount of oil or solvent recovered during the course of the experiments. Generally, experiments involved a solvent phase followed by a non-solvent phase. Non-solvent phases may include more than one stage (i.e., core can be immersed into water or hot water phase and then transferred to wettability alteration phase or vice versa).

Final oil recovery (F_{OR}) was the summation of oil recovered during the solvent phase (O_{RS}) and the oil recovered during the subsequent non-solvent phase (O_{RW}) (water-wettability alteration and/or hot-water phases):

$$F_{OR} = O_{RS} + O_{RW} \quad (1)$$

Oil recovery during the solvent phase (O_{RS}) was estimated by the refractive index measurements and weight difference calculations. Oil recovered during the subsequent non-solvent phase was then calculated using following equation:

$$O_{RW} = F_{OR} - O_{RS} \quad (2)$$

Solvent retrieval amount (S_{RW}) was estimated as a percentage of solvent produced during the non-solvent phase to the amount of solvent that diffused into the core during the solvent phase, which was assumed to be equal to O_{RS} .

$$S_{RW} = \frac{\text{Produced solvent (cc)}}{\text{Oil recovered during solvent phase(cc)}} \quad (3)$$

Note that the cores were put into water/hot-water/wettability alteration phase immediately after the solvent phase and the solvent loss during core transferring process was assumed to be negligible.

It should also be noted here that oil and solvent was produced as a single phase. The produced mixture was called diluted oil recovery (D_{OR}) and was measured continuously against time as % of the pore volume PV:

$$D_{OR} = \frac{\text{Produced solvent (cc)} + \text{Produced oil in non-solvent phase}}{\text{Pore volume (cc)}} \quad (4)$$

The produced oil in the non-solvent phase was obtained from Eq. (2). The produced solvent was then calculated using Eq. (4) and substituted into Eq. (3) to estimate the amount of the solvent retrieved at the end of the process. In many experiments, there was a considerable amount of oil "sticked" to the core surface. This amount was included in the D_{OR} when estimating the produced amount of solvent.

The same soaking period was used in all experiments (10 days) during the solvent phase. Thus, the difference in final oil recoveries can be attributed mainly to the effect of wettability alteration phase. The average oil recovery for solvent in sandstone core samples was $58\% \text{ PV} \pm 3\%$. It was $42\% \text{ PV} \pm 3\%$ for the limestone cases. The results were first analyzed by amount of diluted oil recovery D_{OR} . Next, we provided an estimation of oil recovery and solvent retrieval (S_{RW}) during wettability alteration phase (O_{RW}).

To establish the control cases, a sandstone (core S1) and limestone sample (core L1) were immersed into de-ionized water without any wettability alteration agent for the same time period as the other cores. About 54 % PV of diluted oil was produced from core S1 at the end of 100 days imbibition test, (**Fig. 2**). The following sections will discuss if water at low salinity was the reason behind the improved oil recovery by distilled water in sandstone. Core L1 showed about 2% recovery (**Fig. 3**) indicating that it is strongly oil-wet. The comparisons of different wettability alteration agents with these base cases are provided in the following sections. Note that limestone and sandstone cores were saturated by the same crude oil. The effect of crude oil/rock surface interaction on the wettability of sandstone and carbonate was discussed in different studies, (Anderson 1986; Buckley et al. 1989). It is believed that basic components in crude oil are attracted to the negative sandstone surfaces while acidic components are attracted to the positively charged carbonate. Crude oil used in this study had a relatively high acidic number (0.98 mg KOH/g) and low API (12.6). Considerable amount of asphaltene also participated during the solvent phase, which indicated high asphaltene that might contribute to the oil wetness of the

limestone cores. Buckley and Liu (1998) showed that the acid number and API density may have a direct impact on reversing the wettability of rock surfaces from originally water-wet to oil-wet.

4.2 Sandstone experiments.

4.2.1 *Effect of solvent dilution.* Core S4 was immersed directly into the wettability alteration solution without any solvent treatment, while core S3 was soaked into heptane for 10 days before immersing into the same wettability alteration agent (anionic surfactant STEOL CS 330). **Figure 2a** shows that the amount of oil recovered from core S4 was less than 9 % PV. On the other hand, about 47% PV of oil was produced from core S2. This can also be visualized in **Figure 2b**. The significant role of solvent in the subsequent wettability alteration phase is quite obvious. A similar behavior was observed when solvent was removed by hot-water exposure at 90°C before the wettability alteration phase. After a 10-day soaking period in heptane, core S12 was immersed in hot water for about 4 hours to retrieve solvent diffused into the core during solvent phase. Wettability alteration phase was then applied. Not a single drop of oil was produced after 100 days. In both cases where no solvent exists in the porous medium, anionic surfactant STEOL CS 330 was not efficient. This was recognized earlier by Babadagli (2002) who concluded that surfactants are not feasible for enhanced oil recovery in oil-wet system that contained heavy oil. The effect of solvent dilution, however, may allow benefit of surfactants in such systems.

To study the effect of solvent type, another solvent was tested. Core S5 was soaked into diluent oil for 10 days and then transferred to the wettability alteration phase. Oil recovery was faster than core S3 that immersed in heptane. In fact, with about 63% PV final oil recovery, core S5 yielded the highest recovery among all sandstone cores tested along with core S11 as will be discussed later.

4.2.2 *Effect of chemical solution.* Seven wettability modifying solutions were used in sandstone experiment. When core S1 was immersed into distilled water, about 54% oil was recovered. The ability of low salinity water to alter the wettability of sandstone was pioneered by Tang and Morrow (1997). The recovery was increased to 58% PV for core S3, which was soaked into ethoxylated sulfate anionic surfactant STEOL CS 330 (3 ethylated groups). Salehi et al. (2008) stated that anionic surfactants can remove organic crude oil that adsorbed on the rock surface and thus alter the wettability of sandstone to be more water-wet. As seen, there is a 10% PV difference in diluted oil recovery between core S2 and S3 that were immersed into the same wettability alteration solution. This can be attributed to the complexity of wetting behavior of sandstone, which covers a broader range of wettability than carbonate (Wang et al. 2011).

Oil production during wettability alteration phase for propoxylated sulfate anionic surfactant

ALFOTERRA 145-8S 90 (8 propoxylated groups) and ALFOTERRA 145-4S 90 (8 propoxylated groups) was 30% PV and 28% PV, respectively. One may observe that ethoxylated anionic surfactants are more efficient than propoxylated anionic surfactant in altering the wettability of sandstone toward water-wetness. Although there was no significant difference in oil recovery using Alfoterra 4S or 8S, we observed an alteration of the top surface of core S7 that had immersed in ALFTORRA 145-4S 90.

The performance of ionic liquid 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate BMMIM BF₄ was the best among all wettability modifiers. The use of this imidazolium ionic liquid was inspired by a recent study by Painter et al. (2010) that showed that BMMIM BF₄ is efficient in bitumen separation from oil sand. After recycling BMMIM BF₄ in oil sand sample they were able to recover about 95 % of the bitumen. In this work we used ionic liquid BMMIM BF₄ solution at 50 wt.% to explore how it affects the wettability of sandstone. Oil recovery during the wettability alteration phase for core S11, in which an ionic liquid was applied, was 63% PV. This was the highest recovery in experiment performed using a heptane as solvent. This result encouraged us to use ionic liquid to alter the wettability in limestone at lower concentrations (~0.5 wt.%), which showed positive results as will be explained in the succeeding sections.

Core S14, which soaked into water for 2 weeks and then transferred to alumina oxide nanofluid wettability alteration agent, had 25% PV recovery. We observed that there was accumulation of considerable amount of thick oil on the outer surfaces of core S14. As will be shown later, nanofluids might have a higher impact on fluid-rock properties than fluid–fluid properties. Among the two alkaline solutions tested, NaBO₂ had a better oil recovery (60% PV) with about 13% increase over NaOH solution. A study by Zhang et al. (2008) also showed the positive impact of NaBO₂ but on carbonate core samples. It was very interesting to see this relatively low cost chemical having the best diluted oil recovery among other chemicals similar to ionic liquid BMMIM BF₄. Even though it is generally understood that increasing the pH of the solution reduces the positive charges on the carbonate and thus enhances the repulsion between oil-wet organic components and the carbonate surface, it is not clear why NaBO₂ have a higher efficiency than other alkaline solutions in altering the wettability of sandstone. The mechanism of wettability alteration by NaBO₂ is currently under investigation.

Visual comparisons of wettability alteration phase for different sandstone samples are presented in **Figure 2c**. One can pay a closer look at the outer surfaces of these cores at the end of wettability alteration phase in **Figure 2d**. In **Figure 2e** and **Figure 2f**, spontaneous imbibition and top surfaces of core that exposed to ALFOTERRA surfactants can be observed, respectively. It is obvious that there was a modification to the surface of core S7 that had immersed in ALFTORRA

145-4S 90 was occurred. An emulsive substance that might be a mixture of asphaltene, clay, and surfactant was released from the top surface. Both surfactants are branched alcohol propoxy sulfates but have different structure.

4.2.3 Effect of temperature. To study the effect of the temperature on the process, core S10 was immersed into water at 25°C for 16 days. The temperature was then increased to 65°C. The oil recovery increased sharply from 8% PV during the cold water phase and peaked at 33% after two weeks at hot-water phase. The recovery was then leveled off and no significant oil was produced after the two-week period. The main mechanism of the diluted oil recovery during this period was the solvent pushing force while it was leaving the core under the influence of temperature. Spontaneous imbibition and the top surface of core S10 are presented in **Figure 2g** and **Figure 2h**, respectively.

4.2.4 Oil recovery and solvent retrieval. Figure 2e displays the oil recovery during the non-solvent phase (water/wettability alteration /hot-water) and solvent retrieval at the end of experiments. It can be seen that core S4, which had no solvent phase, exhibited the highest oil recovery (46% PV). This was expected as it had a higher residual oil than other cores that were exposed to solvent phase. About 58% PV \pm 3% was recovered during the solvent phase leaving less than 50% PV while core S6 was 100% saturated during the wettability alteration phase. Among other cores, core S10, which was exposed to moderately high temperate water (65°C), had the highest oil recovery with about 32% PV.

As will be shown later, there is an agreement in sandstone and limestone results regarding their highly positive response to thermal phase at moderately low temperature (60°C). Note that oil recovery for core S12, which was also exposed to a thermal phase at higher temperature, recovered a lower amount of oil (26% PV). Hence, it is better to apply moderately low temperature to benefit from the solvent pushing force. If the temperature is increased to be close to the bubble point of the solvent, the solvent will be retrieved very fast but no significant contribution of the solvent boiling force on the oil recovery is expected. It is also interesting to observe that the ionic liquid was able to recover most of the solvent in core S11; however, it also recovered the least amount of oil. In fact, this observation is in line with previous observation about the solvent retrieval at low and moderate temperate. These observations indicate that faster solvent retrieval may results in less oil recovery. This not only confirms the importance of solvent in the type of porous medium, it also signifies how critical the solvent retrieval process is and its role to contribute to the oil recovery. In short, the process of solvent retrieval should be optimized to benefit from its pushing boiling forces in oil-recovery.

Ethoxylated anionic surfactants CS 330 (core S2 and core S3) add (24-26% PV) oil recovery,

which is the same range of recovery with distilled water (core S7) .The oil recovery was 27% PV. Using diluent oil as a solvent did not seem to change this figure substantially; about 26% PV of oil was recovered. Note that about 2-3% of this recovery produced by the hot-water phase that was applied at the end of experiment. Only 3% of solvent was retrieved by hot-water. The inefficiency of hot-water phase could be attributed to low residual oil and solvent at the end of solvent retrieval phase. There is a noticeable difference in oil recovery of propoxylated surfactant 4S (core S7) and 8S (core S6). Propoxylated surfactant 4S had about 20% PV oil recovery. As explained earlier, there was ongoing modification on the top surface of core due to the interaction of surface minerals with 4S surfactant. This might be translated into about 4% more oil recovery than surfactants 8S. Alumina nanofluid (core S13) was not able to retrieve solvent efficiently, however, a thick layer of oil accumulated at the outer surfaces. As can be seen in **Figure 2e**, this increases the oil recovery but not the solvent retrieval. Thus, the dilution of original heavy oil with solvent did not affect the way of alumina interacted with fluids in the core. On the other hand, it might have a substantial impact on the rock surface properties. Using high pH solution, NaBO₂ (core S15) as a wettability modifier was shown to have a positive effect on the diluted oil recovery. Retrieved solvent seems to comprise considerable percentage of the diluted oil recovery. The 63% solvent retrieval indicates wettability alteration of carbonate to more water-wet. NaOH solution (core S14) was also able to contribute to the solvent retrieval by 43%.

Overall, this break down of diluted oil recovery during the non-solvent phases shows the difference in the "type" of oil that can be produced by different wettability modifiers. The faster the diluted oil recovery, the higher the chances that it will be composed mainly of the light solvent that had been injected in the previous phase. Whether it is solvent or oil, using wettability alteration agents was shown to be an effective means to contribute to oil-recovery by solvent injection as it offers the possibility to retrieve back up to 90% of the solvent without the need for a thermal phase. This will also be accompanied with additional oil recovery.

4.3 Limestone experiments.

4.3.1 Effect of solvent dilution. **Figure 3a** shows that almost no oil was recovered from core L3, which was not exposed to a solvent phase. Similar behavior was observed in core L10, which had most of the solvent retrieved by applying “hot water phase” before the wettability alteration phase. The recovery in the base case L2 was about 40% PV indicating the importance of the solvent phase. These results agree with sandstone experiment in showing the importance of the solvent phase to any chemical treatment for oil-wet systems containing heavy oil. In the carbonate cores, the recovery of diluted oil is even low due to the stronger oil-wetness compared with sandstone.

4.3.2 Effect of chemical solution. Among all wettability modifiers that were tested, the

performance of cationic surfactant C12TAB was among the best. After 100 days, almost 40% PV was produced from core L2, which was immersed into a cationic surfactant solution (dodecyl trimethylammonium bromide, C12TAB). Wettability alteration by ionic-pair interaction was suggested as the main mechanism of improved oil recovery by cationic surfactants in carbonate (Standnes and Austad 2000). To test the reproducibility of the data, experiment L2 was repeated in L14. Diluted oil recovery was 38% PV with a 2% PV difference from L2. Core L4, which was soaked into another alkyl ammonium cationic surfactant (ARQUAD) for the same period, produced about 17%. Anionic surfactants (STEOL CS 330) were used at low concentration 1mmole/l (~0.004 wt.%) for core L6. Diluted oil recovery was about 25%. When core L6 was immersed into alkaline anionic surfactant solution (Na_2CO_3 -STEOL CS 330), the concentration of STEOL CS 330 was about 0.05 wt.%. Phase behavior tests were conducted and indicated that optimal salinity lied in the range of 0.12-0.15 wt.% Na_2CO_3 . The recovery when using (0.12 wt.% Na_2CO_3 -0.05 wt.% STEOL CS 330) was about 10% PV, which is far less than the previous case (0.004 wt.% STEOL CS 330). This might be attributed to lower interfacial tension obtained when surfactant concentration was increased, which reduced the efficiency of capillary imbibition.

Although surfactant adsorption is reduced when Na_2CO_3 is used, there is no significant impact of adding Na_2CO_3 to surfactant solution (Zhang et al. 2008) on oil recovery. Three types of nanofluids were used in this research. Al_2O_3 , ZrO_2 , and SiO_2 nanoparticles were dispersed in distilled water using ultrasonic for about 30 minutes. Alumina and silica were relatively stable during the imbibition test. Zirconium nanodispersion became partially unstable after about 4 weeks. There was almost no oil recovery in the core that was exposed to alumina nanofluid. Zirconium nanofluid, on the other hand, showed some encouraging results. Core L12, which was immersed into water for 12 days and then placed into zirconium oxide nanofluid solution, produced about 25 % PV. Silica nanofluid was also investigated. Although no significant imbibition was observed, there was a thick layer of oil at the outer surfaces of the core. High pH solution NaBO_2 was tested on core L20. Diluted oil recovery improved to 34% after 74 days of spontaneous imbibition. The efficiency of alkaline NaBO_2 solution as a wettability modifier is enhanced by the fact that it provides lower cost alternatives to other expensive chemicals.

Ionic liquid [BMMIM][BF_4] showed positive results with sandstone and therefore it was tested for limestone at low concentrations. When BMMIM BF_4 was used for wettability alteration phase in core L9 at 1 wt.%, it was able to produce about 48% PV, which was the highest diluted oil recovery in limestone experiments. This result showed that BMMIM BF_4 can be a promising wettability modifier for carbonate. Ionic liquid can influence the fluid-fluid interaction. It reduces the interfacial tension of water at low concentration, Malham et. al (2006). It can also affect the rock-fluid properties as it decreases the adhesive force between rock surface and crude oil

(Hoshead et. al. 2010). We can conclude that ionic liquids alter the wettability of rock surface by two means: IFT reduction and by decreasing the adhesive forces between rock and the adsorbed organic component on the rock surface. Investigation of the mechanisms by which ionic liquid alter the wettability is ongoing.

Visual comparisons of six wettability alteration cases of limestone are presented in **Figure 3b**. Outer Surfaces of three limestone cores at the end of wettability alteration phase are provided in **Figure 3c**. **Figure 3d** shows the effect of silica nanoparticles on limestone core surface.

Five more experiments were conducted using ionic liquids. The concentration was varied from 0.1 wt % to 50 wt.%. Note that Painter et al. (2010) used pure ionic liquid in their experimental work of oil sand separation with BMMIM BF₄. The feasibility of using such high concentration was justified by the ability to recycle the ionic liquid during the separation process. The use of ionic liquid in this work is substantially different and therefore no pure ionic liquid was used. The maximum concentration during this study was 50 wt. % and was only used to test the extreme effect of ionic liquid concentration.

As seen in **Figure 3e**, the diluted oil recovery was improved when concentration was increased from 0.1 wt. % (core L15) to 0.5 wt.% (L16). At 0.5 wt.%, recovery went up to 49%, which was the best diluted oil recovery in all experiments. The concentration was increased to 3 wt.% for L17 and then to 50 wt.% for L18. Recovery was reduced while increasing the concentration. These results show that there is an optimum concentration for ionic liquid, which would probably be in the range of 0.5 to 1.0 wt.%. Another imidazolium ionic liquid was tested in this investigation. 1-butyl-3-methylimidazolium tetrafluoroborate BMIM BF₄ at 1.0 wt.% was used in core L19. About 36% PV of oil was produced after 74 days of spontaneous imbibition.

4.3.2 Effect of temperature. Cores L7 and L8 were put into brine for a period of time before applying wettability alteration phase. No oil was produced from core L7 during 13 days soaking period. The core was then immersed immediately in brine that contained divalent ions (Ca⁺², Mg⁺², SO₄⁻²) at 25°C for 3 days and no oil was produced, indicating no change in wettability. When temperature was increased to 65°C, droplets of oil started to come out of the core after 2 hours and recovery reached 28% PV after 6 days and became stable at this value. For core L8, the soaking period in water at 25°C was 16 days and the temperature was then increased to 65°C. The oil recovery was observed to reach 20% after 7 days. No more oil was recovered after this period.

4.3.3 Oil recovery and solvent retrieval. Oil recoveries during the non-solvent phase and solvent retrieval are illustrated in **Figure 3f**. Generally, the limestone cores exhibited lower recoveries than sandstones. Only 4% of solvent was retrieved for core L1, which was immersed in distilled

water. Solvent retrieval was increased to 46% when C12TAB surfactant was used. Oil recovery, on the other hand, was also increased from 20% PV to 32% PV. For surfactant solutions core L4, L5, and L6, the range of oil recoveries lied between 23 and 29% PV. The lowest oil recovery was seen in core L3, which had no solvent phase.

Experiments that involved a hot-water phase at moderate high temperature (60°C), L7 and L8 showed improved oil recovery of about 32-34%. As discussed earlier, solvent pushing force was the main mechanism of oil recovery. Therefore, there was no significant influence of divalent ions at increasing the oil recovery and, similar to sandstone experiments, this range of temperature was more efficient in increasing oil recovery than high temperature.

When all solvent was recovered by high temperature (90°C), then cold water phase was applied. Oil recovery was about 27%. The highest oil recovery in all experiments was observed in L9, which was immersed in ionic liquid BMMIM BF₄. About 37% of oil in place was recovered by the ionic liquid solution at 1 wt.% Solvent retrieval was also considerably high (45%). Solvent retrieval was also at this range for zirconium nanofluid. About 41% of the solvent was retrieved. Other tested nanofluid (alumina and silica) were inefficient in term of solvent retrieval. While the highest oil recovery was seen in 1 wt.% ionic liquid BMMIM BF₄, the same ionic liquid was able to produce back 81% of the solvent diffused into the rock in core L18 when the concentration was considerably high (50 wt.%). Note that oil recovery was relatively low at this high concentration. While solvent retrieval for core L16, which immersed in 0.5 wt. BMMIM BF₄ ionic liquid solution, was at the same range of core L17, which was immersed in 3 wt.% (57 and 58% respectively), higher oil recovery was observed at the lowest concentration. Imidazlium ionic liquid BMIM BF₄ also showed a tendency to improve oil recovery by wettability alteration similar to NaBO₂ solution. Oil recovery was 29% for core L19 (BMIM BF₄) and 28% for L20. Solvent retrieval was 32% for BMIM BF₄ and 31% for high pH solution.

Figures 2 and 3 present the ultimate recoveries by spontaneous imbibition as a wettability alteration index. To observe the behavior of imbibition recoveries, **Figures 4 and 5** are also provided for the limestone and sandstone cases, respectively. As seen in **Figure 4a**, some cases present a quick jump in the recoveries (cores L2, L14, and L20) and good ultimate recoveries as a quick and strong change in the wettability. It is also clear that L9 had a distinguished higher performance than other chemicals. Starting from the third week of imbibition, diluted oil recovery by ionic liquid was increasing substantially. One reason for this push in recovery can be the alteration of matrix wettability toward water-wetness. Also, there was a contribution of gravity forces, which usually takes place at a later time than capillary forces. A different regime for oil production was also observed. Oil production by cationic surfactant C12TAB (L2) was in the form

of small droplets of oils from all core surfaces while for ionic liquid big droplets of oil were formed and then detached from the core surface. Oil was produced from all the surfaces; however, considerable amount was recovered from the top surface, which also confirms the participation of buoyancy forces. Cores L5 and L12 presented a slow change in wettability but improved at the late stage.

As mentioned earlier, core L7 and L8 were exposed to a different sequence of phases. **Figure 4b** illustrates the change in recovery with time for core L7 at different stages, taking into account the effect of temperature. Similarly, the plot in **Figure 4c** shows a jump in recovery after increasing the temperature of water to 65°C for core L8.

Experiments L15 to L19 are displayed in **Figure 3e**. These images show the effect of concentration for ionic liquid BMMIM BF₄. When the concentration was 0.1 wt.%, the diluted oil recovery was slow but increased with time. When the concentration was increased to 0.5 wt.%, there was a quick jump in the speed of the recovery. The ultimate oil recovery was also higher than 0.1 wt.%. Ultimate diluted oil recovery was not changed when the concentration was further increased to 1 wt. %, but the recovery was faster. The speed of the recovery was enhanced more when the concentration became 3 wt.%, however, the ultimate oil recovery was reduced. Increasing the concentration to 50 wt.% neither improves the rate of recovery nor the ultimate produced amount of diluted oil.

The recovery trends in the sandstone experiments can be classified under three groups. (1) Core S2, S5, S9, and S11 represent the best case scenarios due to the highest ultimate recovery (**Fig. 5a**). Initial recovery rates were also fast for these cases. (2) Cores S1, S3, S10, S14, and S15 the oil recovery was lower than the first group initially and then started increasing rapidly. (3) In the rest of the cores it took a longer time before the imbibition recoveries started and no significant wettability alteration was achieved. The change in imbibition curve with time upon replacing chemical solution in core S9 (STEOL CS 330) with deionized water is provided in **Figure 5b**, while **Figure 5c** shows the rise recovery when the temperature was increased to 65°C for core S10. Although the ultimate recoveries from these experiments can be used as a good indication of wettability alteration, the shape of the recovery curves can be used to further analyze the wettability alteration (and possibly other chemical and physico-chemical) process.

5. Conclusions

- A wide range of wettability alteration chemicals suggested in literature for light oil systems were tested on heavy-oil saturated weakly water-wet sandstones and oil-wet

limestones that were exposed to solvent treatment. These chemicals include anionic and cationic surfactants, nanofluids, high pH solutions, and ionic liquids.

- No wettability alteration was encountered using alumina nanofluid in limestone. On the other hand, evidence of some degree of wettability alteration was observed in sandstone when using alumina nanofluid. For limestone, zirconium oxide nanofluids were observed to alter wettability. Silica nanofluid did not imbibe into the limestone; however, it affected the rock surface properties.
- Solvent treatment improves the wettability alteration process in NFWOR by viscosity and density reduction. If no solvent was introduced to the matrix system or the solvent was retrieved, chemical treatment for wettability alteration is expected to be a very slow process.
- The best wettability modifiers for weakly water-wet sandstone were found to be anionic surfactants, high pH solution, and ionic liquids. Alternate injection of solvent and moderately hot water can be considered wettability alteration process. Solvent treatment with diluent oil increases the efficiency of wettability modification by chemical solution better than heptane.
- Cationic surfactant, high pH solutions, and ionic liquids altered the wettability of oil-wet limestone better than other chemical solutions. The effect of anionic surfactant and ionic liquid is under investigation for a clarification of their ability to modify the wettability of limestone toward water-wetness.
- Solvent can be retrieved using non-thermal methods. Up to 80 % of solvent can be retrieved by wettability alteration.
- Imidazolium ionic liquids tested in this study were efficiently successful in wettability alteration of oil-wet sandstone and limestone. Oil is recovered by gravity forces and capillary imbibition.
- There is an optimum concentration of ionic liquid at which both oil rate and ultimate oil recovery reaches the maximum. In this study, the optimum concentration is found to be in the range of (0.5 to 1.0 wt.%).
- High pH solution NaBO_2 can improve oil recovery in Grosmont carbonate if it is accompanied with solvent phase.

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TABLE 1: Rock sample properties

<u>Rock Type/ Properties</u>	<u>Porosity (%)</u>	<u>Permeability (md)</u>	<u>Length (inch)</u>	<u>Diameter (inch)</u>	<u>Average Pore Volume (cc)</u>
Berea sandstone	19-21	200-500	3.5	1.5	19
Indiana limestone	19-21	10-40	3.5	1.5	19

TABLE 2: Properties of crude oil, diluent oil, and heptane

<u>Materials/ Properties</u>	<u>Density (gm./cc) at 25 °C</u>	<u>Viscosity (cp.) at 25 °C</u>	<u>Acid Number KOH /g</u>
Crude oil	0.9819	3,600 cp	0.98 mg
Heptane	0.684	0.386	-
Diluent oil	0.738	0.742	-

TABLE 3: Wettability alteration chemical solutions

<u>No</u>	<u>Chemical Type</u>	<u>Chemical Name</u>	<u>Concentration</u>	<u>Reference in Literature</u>
1	Anionic surfactant	STEOL CS 330	1mmole/l	Salehi et al. 2008
2	Anionic surfactant	ALFOTERRA 145-8S 90	1mmole/l	Elmofty 2012
3	Anionic surfactant	ALFOTERRA 145-4S 90	1mmole/l	Elmofty 2012
4	Alkaline anionic surfactant	Na ₂ CO ₃ STEOL CS 330	0.15 wt.% Na ₂ CO ₃ 0.05 wt.% STEOLCS 330	Hirasaki and Zhang 2003
5	Cationic surfactant	C12TAB	1 wt. %	Standnes and Austad 2000
6	Cationic surfactant	ARQUAD 2C-75	1 wt. %	Standnes and Austad 2003
7	Ionic liquid	[Bmmim][BF ₄]	(0.1, 0.5, 1.0,3,50 wt.%)	Painter et al. 2010
8	Ionic liquid	[Bmim][BF ₄]	1.0 wt. %	-
9	Nanofluid	Al ₂ O ₃ 30 nm	500 ppm	Giraldo et al. 2013
10	Nanofluid	ZrO ₂ (45-55nm)	1 wt. %	Ali Karimi et al. 2012
11	Nanofluid	SiO ₂	1 wt. %	Maghzi et al. 2011
12	High PH solution	NaOH	2.5 wt. %	Zhang et al. 2008
13	High PH solution	NBO ₂	2.5 wt. %	Zhang et al. 2008
14	Divalent ions solution	CaCl ₂ ,MgCl ₂ ,NaCl,Na ₂ SO ₄	See table 4	Gupta and Mohanty 2011

Table 4: Chemical Composition of brine used in limestone experiment L7 (Gupta and Mohanty 2011)

<u>Chemical</u>	<u>CaCl₂ (g/l)</u>	<u>MgCl₂ (g/l)</u>	<u>NaCl(g/l)</u>	<u>Na₂SO₄ (g/l)</u>
Concentration	0.942	4.65	15	14.2

Table 5: Sandstone experiments

Core Number	Wettability	Solvent Type	Sequence type
Core #S1	Weakly water-wet	Heptane	Solvent (at 25°C for 10days) – Water (at 25°C for 100 days)
Core #S2	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days – STEOL CS 330 (at 25°C for 100 days)
Core #S3	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days) – STEOL CS 330 (at 25°C for 100 days)
Core #S4	Weakly water-wet	Heptane	STEOL CS 330 (at 25°C for 100 days)
Core #S5	Weakly water-wet	Diluent oil	Solvent (at 25°C for 10 days) – STEOL CS 330 (at 25°C for 100 days)
Core #S6	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days) – ALFOTERRA 8S (at 25°C for 100 days)
Core #S7	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days) – ALFOTERRA 4S (at 25°C for 100 days)
Core #S8	Water-wet	Heptane	Solvent (at 25°C for 10 days) – STEOL CS 330 (at 25°C for 100 days)
Core #S9	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days) – STEOL CS 330 (at 25°C for 13 days) - Deionized Water (at 25°C for 87 days)
Core #S10	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days) -Water (at 25°C for 16 days)– Water (at 65°C for 84 days)
Core # S11	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days) – Ionic Liquid (at 25°C for 100 days)
Core #S12	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days) – Hot water (at 90°C for 4 hours) – STEOL CS 330 (at 25°C for 100 days)
Core #S13	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days) – Water (at 25°C for 13days) - Alumina oxide nanofluids (at 25° C for 87 days)
Core #S14	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days) – NaOH (at 25°C for 100 days)
Core #S15	Weakly water-wet	Heptane	Solvent (at 25°C for 10 days) – NaBO ₂ (100 days)

Table 6: Limestone experiments

Core Number	Wettability	Solvent Type	Sequence type
Core #L1	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Water (at 25°C for 100 days)
Core #L2	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – C12TAB (at 25°C for 100days)
Core #L3	Oil-Wet	Heptane	C12TAB (at 25°C for 100 days)
Core #L4	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – ARQUAD 2C-75 (at 25°C for 100 days)
Core #L5	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – STEOL CS 330 (at 25°C for 100 days)
Core #L6	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – STEOL CS 330 + Na ₂ CO ₃ (at 25°C for 100 days)
Core #L7	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Water (at 25°C for 13days) -(Ca ⁺² ,Mg ⁺² ,SO ₄ ⁻²) Solution (at 25°C for 3 days) -(Ca ⁺² ,Mg ⁺² ,SO ₄ ⁻²) Solution(at 65°C for 84 days)
Core #L8	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Water (at 25°C for 16 days) – Water (at 65°C for 84 days)
Core #L9	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Ionic Liquid BMMIM BF ₄ (1 wt. %) (at 25°C for 100 days)
Core #L10	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Water (at 90 °C for 4 hours) - C12TAB (at 25°C for 100 days)
Core # L11	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Distilled water (at 25°C for 13days) -Alumina oxide nanofluid (at 25°C for 87 days)
Core #L12	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Distilled water (at 25° C for 13days)-Zirconium oxide nanofluid (at 25° C for 87 days)
Core #L13	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) –Silicon oxide nanofluid (at 25°C for 74 days)
Core #L14	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – C12TAB (at 25°C for 100 days)
Core #L15	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Ionic Liquid BMMIM BF ₄ (0.1 wt. %) (at 25°C for 100 days)
Core #L16	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Ionic Liquid BMMIM BF ₄ (0.5 wt. %) (at 25°C for 100 days)
Core #L17	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Ionic Liquid BMMIM BF ₄ (3 wt. %) (at 25°C for 100 days)
Core #L18	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Ionic Liquid BMMIM BF ₄ (50 wt. %) (at 25°C for 100 days)
Core #L19	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – Ionic Liquid BMIM BF ₄ (1 wt. %) (at 25°C for 74 days)
Core #L20	Oil-Wet	Heptane	Solvent (at 25°C for 10 days) – NaBO ₂ (74 days)

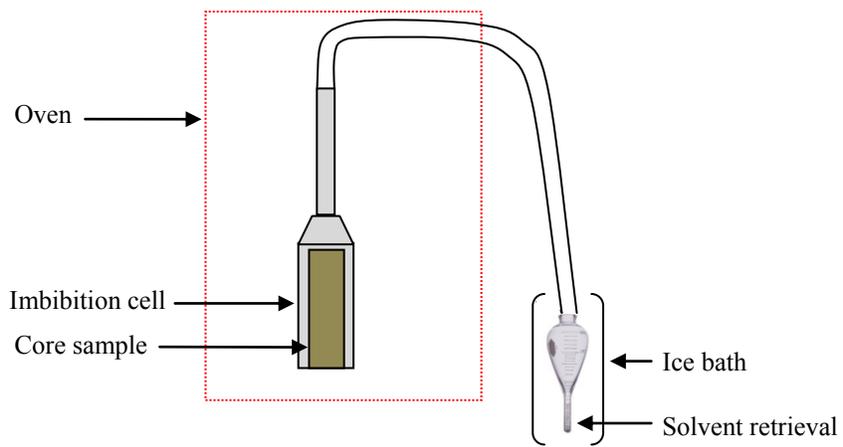


Figure 1: Experimental setup for solvent retrieval “hot water phase”.

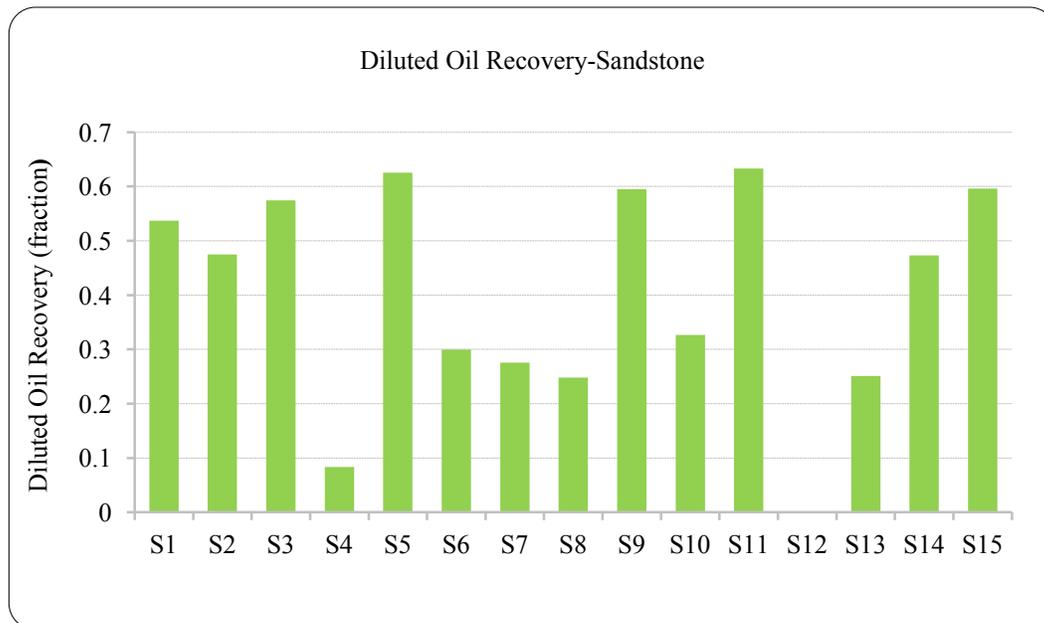


Figure 2a: Diluted oil recovery in sandstone cores.



Core # S2

Core # S4

Figure 2b: Comparison of wettability alteration phase in core #S2 and #S4.



Core #S12

Core #S4

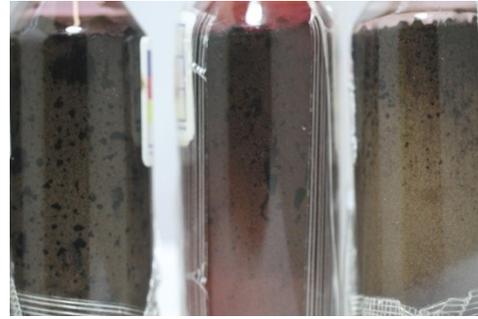
Core # S1

Core # S11

Core # S2

Core #S5

Figure 2c: Comparison of six wettability alteration chemicals for the sandstone samples.



Core #S12 Core #S4 Core #S1 Core #S11 Core #S2 Core #S5
Figure 2d: Comparison of outer surfaces of different sandstone samples at the end of wettability alteration phase.



Core #S6 Core #S7
Figure 2e: Comparison of two surfactants: ALFOTERRA 145-8S 90 (left) and ALFOTERRA 145-4S 90 (right): Oil recovery.



Core #S6 Core #S7
Fig. 2f—Comparison of two surfactants ALFOTERRA 145-84S 90 (left) and ALFOTERRA 145-4S 90 (right): Top surfaces.



Core #S10

Figure 2g: Wettability alteration phase for the sandstone sample at 65° C (oil recovery).



Core # S10

Figure 2h: Wettability alteration phase for the sandstone sample at 65°C (top surface).

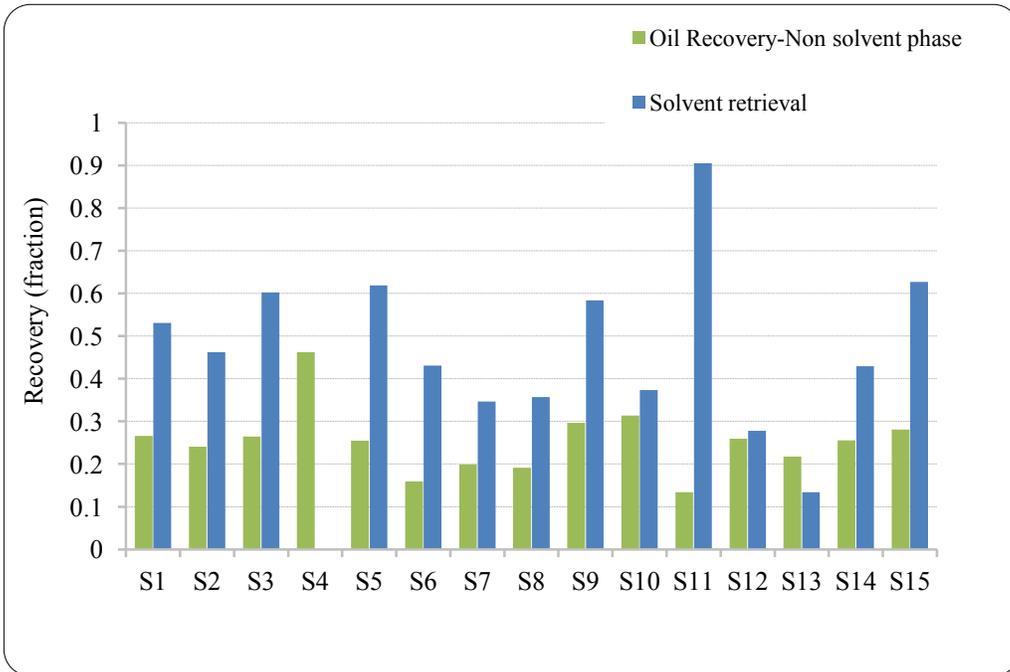


Figure 2i: Oil recovery during the non-solvent phase and solvent retrieval at the end of experiments.

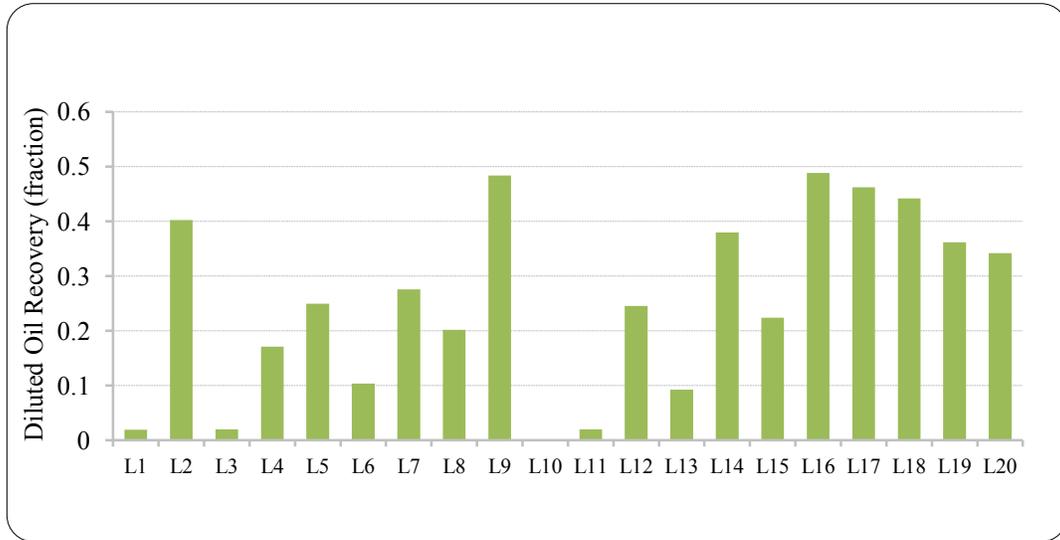


Figure 3a: Final diluted oil recovery in limestone cores.



Core #L10 Core #L5 Core #L1 Core #L18 Core #L2 Core #L3
Figure 3b: Comparison of six wettability alteration chemicals for the limestone samples.



Core #L18 Core #L2 Core # L3
Figure 3c: Comparison of outer surfaces of different limestone samples at the end of wettability alteration

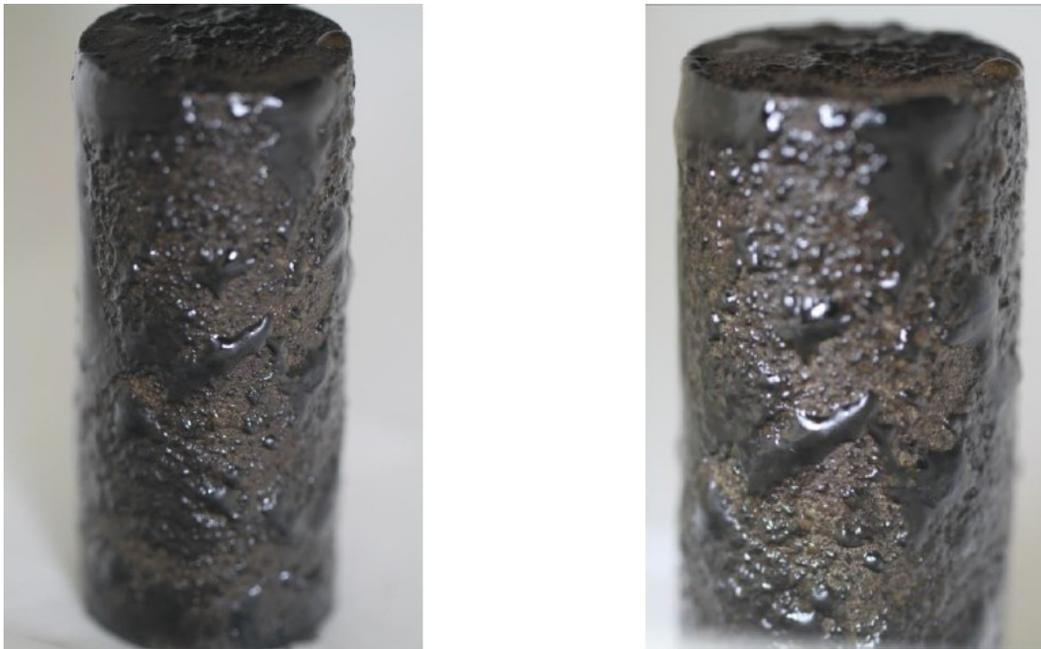


Figure 3d: The effect on silica nanoparticles on limestone core surface.

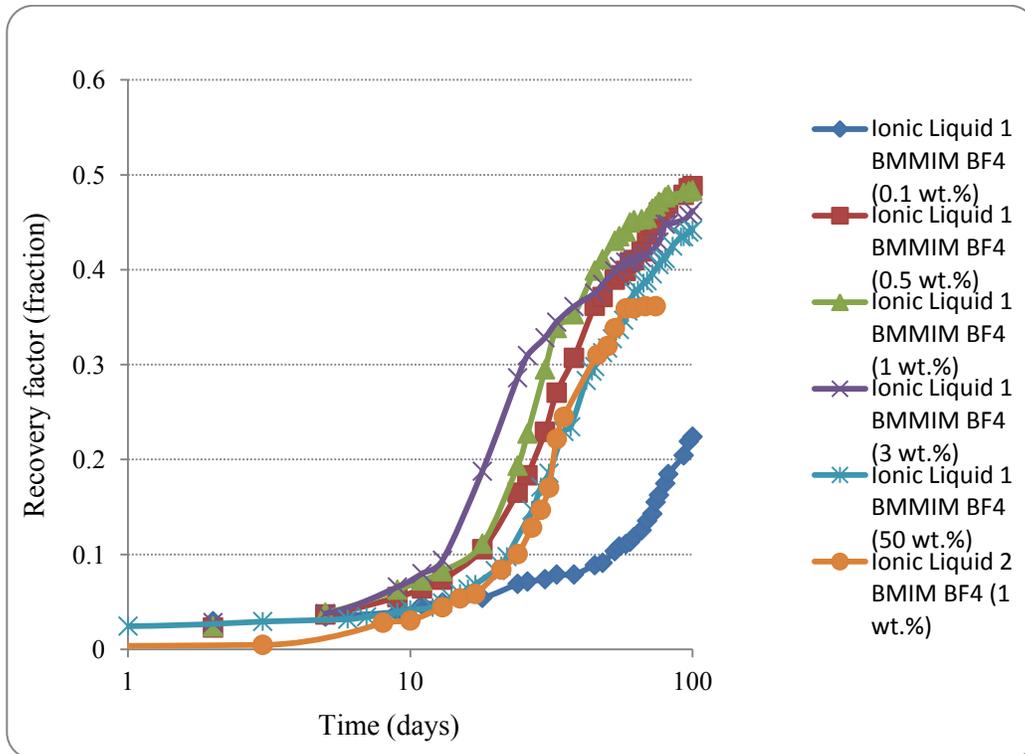


Figure 3e: Diluted oil recovery during wettability alteration phase for ionic liquids.

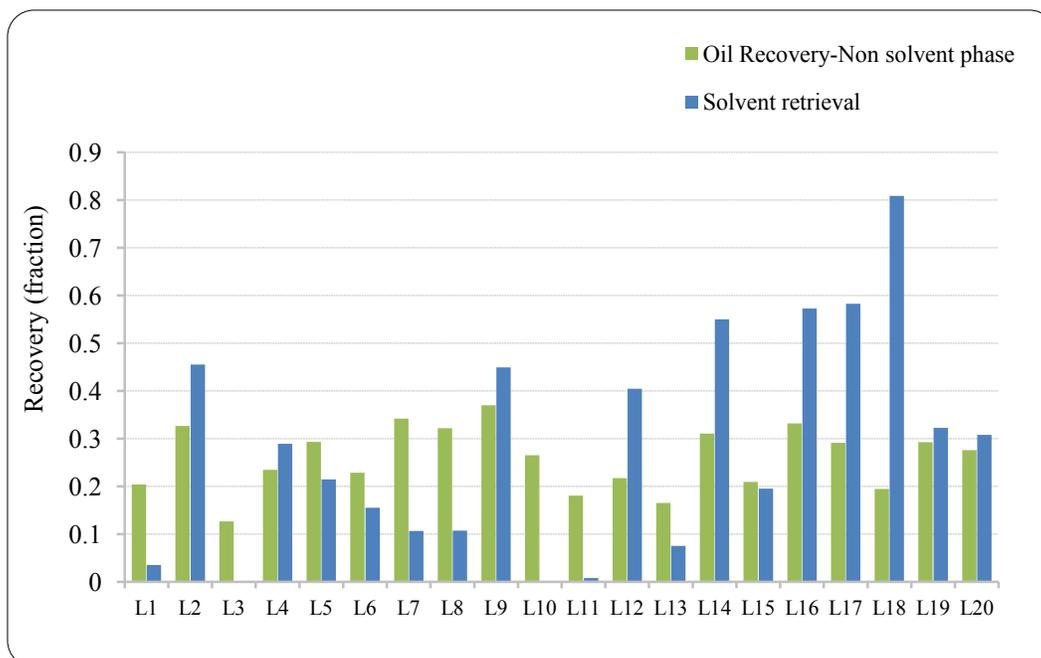


Figure 3f: Oil recovery during the non-solvent phase and solvent retrieval at the end of experiment.

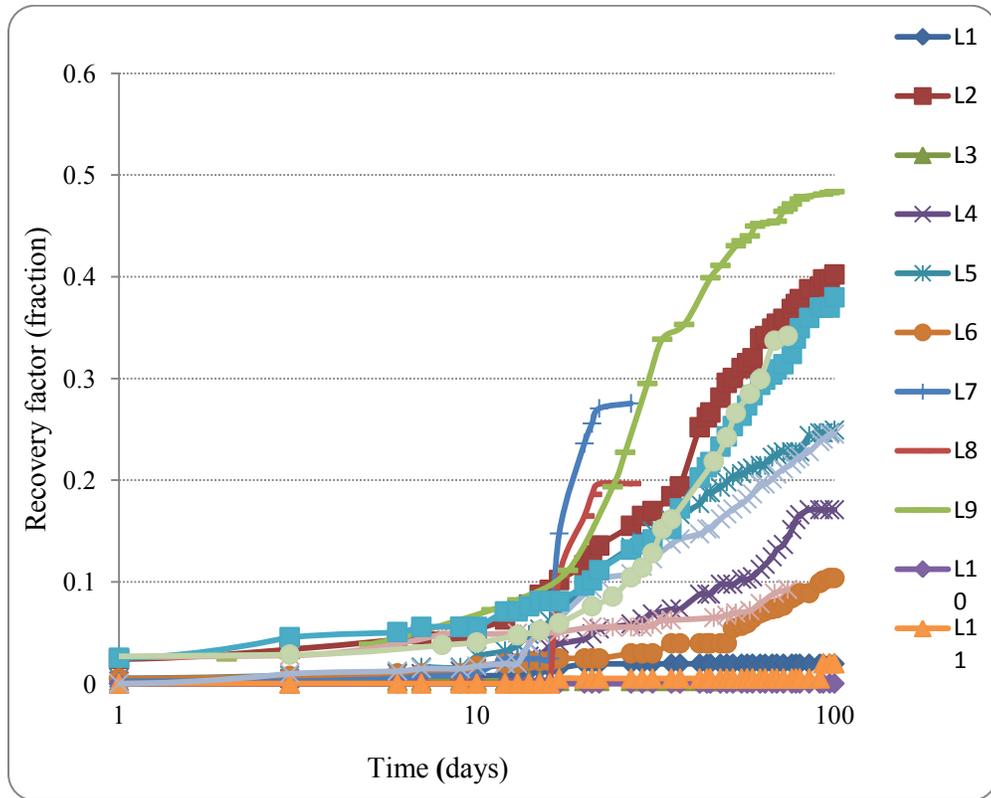


Figure 4a: Diluted oil recovery in limestone cores.

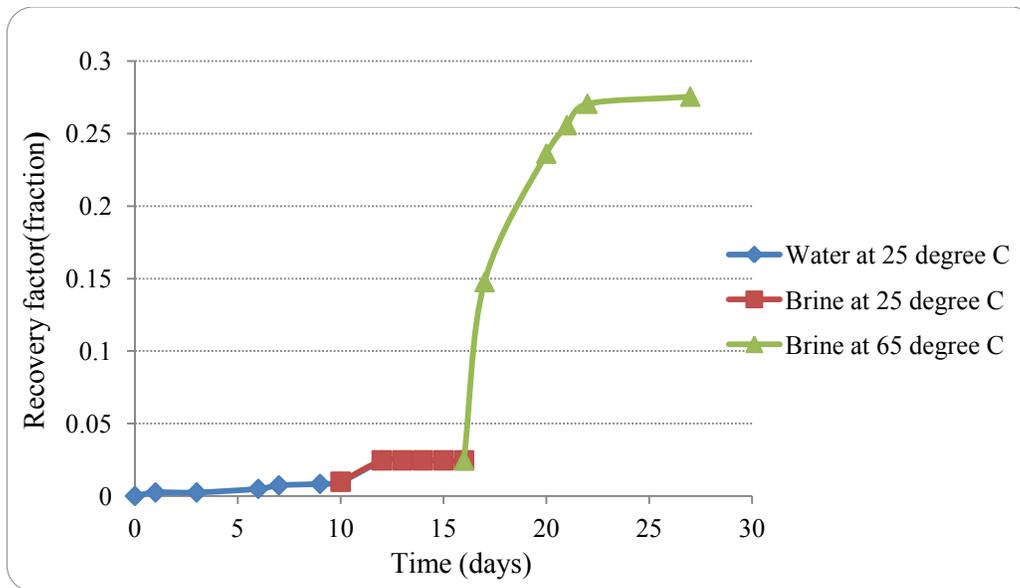


Figure 4b: Diluted oil recovery in limestone core #L7.

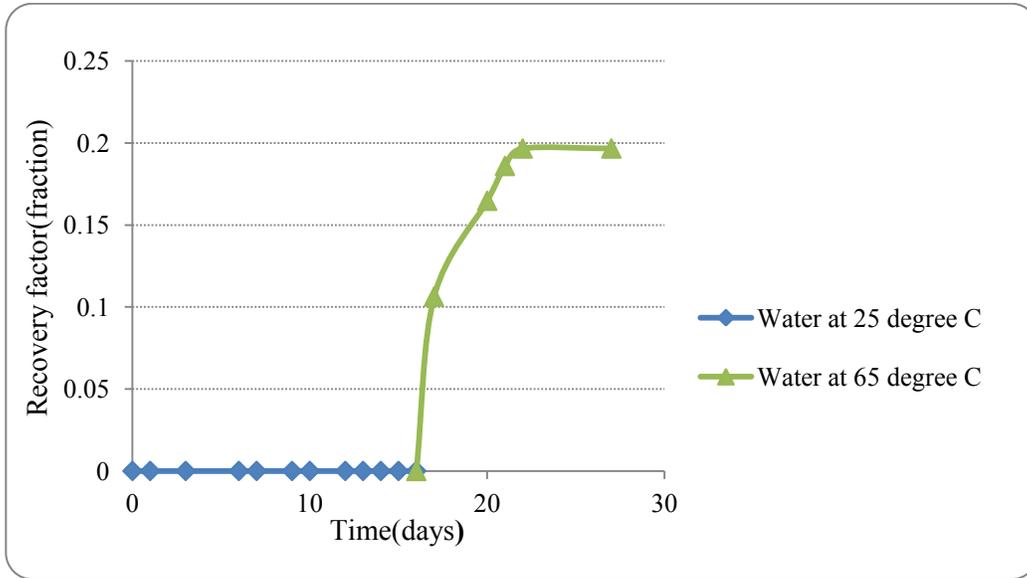


Figure 4c: Diluted oil recovery in limestone core#L8.

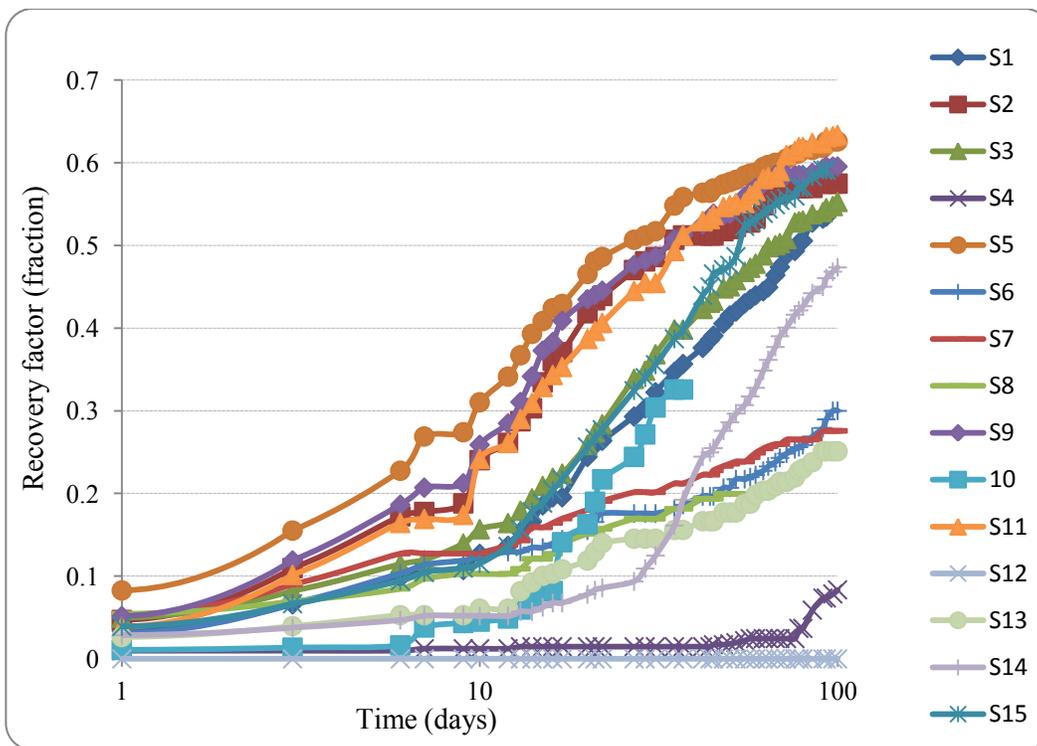


Figure 5a: Diluted oil recovery in sandstone cores.

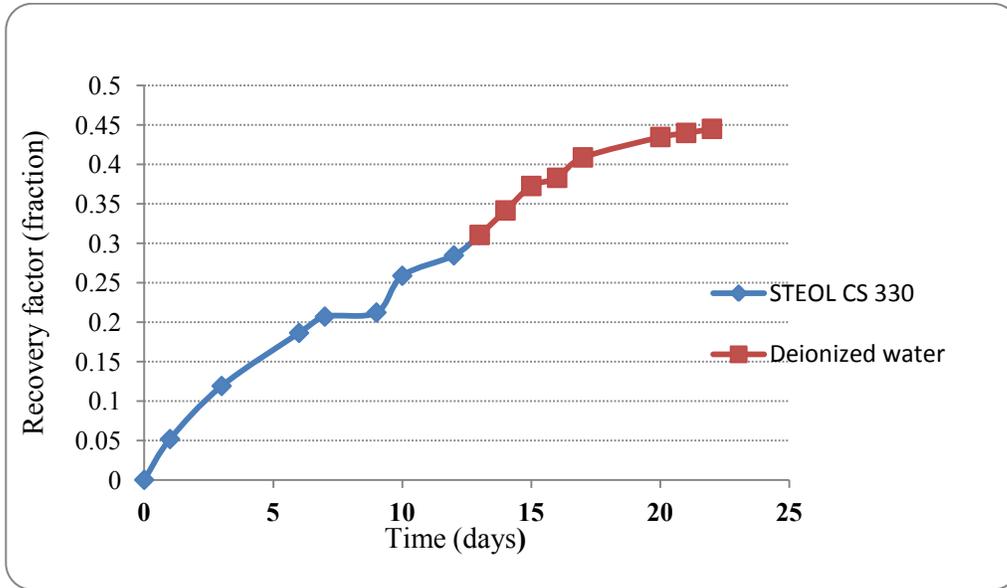


Figure 5b: Diluted oil recovery in sandstone core#S9.

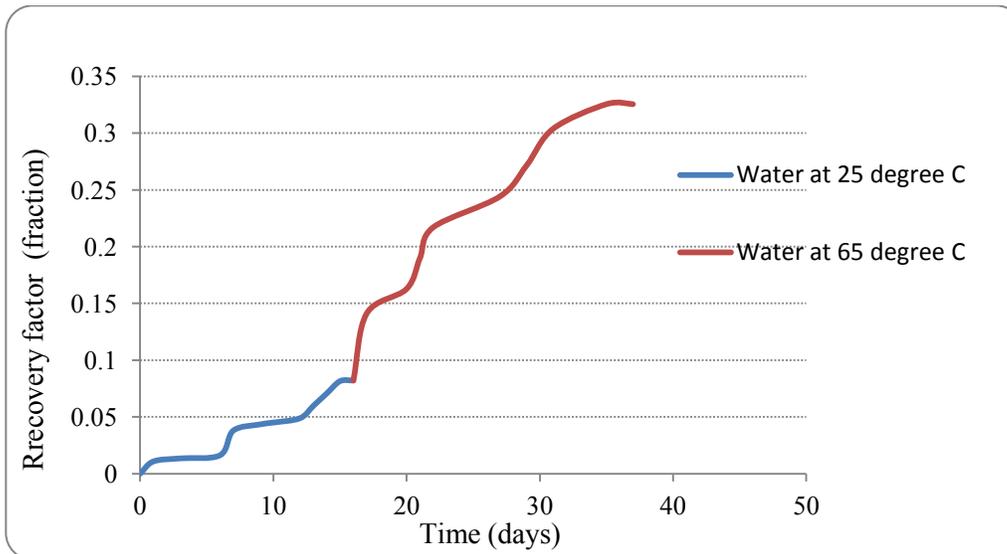


Figure 5c: Diluted oil recovery in sandstone core#S10.



Figure 6a: Grosmont carbonate core sample.



Figure 6b: Wettability alteration phase for Grosmont core.

CHAPTER 5: CONTRIBUTION AND RECOMMENDATIONS

Contributions

1. A new experimental setup was designed to quantify solvent retrieval during hot-water phase of the SOS-FR method.
2. The effect of the rock properties (wettability and permeability), oil viscosity, and matrix boundary conditions on the process were revealed.
3. Oil recovery and solvent retrieval during SOS-FR were optimized based on key parameters including solvent type, solvent soaking period, cycle numbers and durations, and temperature during hot/water phase.
4. A critical review of the past literature in wettability alteration in sandstone and limestone was presented to fill the gap in this field. About 100 published papers were covered with a comprehensive analysis of materials/methods suggested for different types of reservoirs. Generally, the following systematic steps were followed to improve oil recovery in oil-wet reservoirs:
 - Establish the mechanisms that shifted the wettability to be oil-wet
 - Determine the reservoir and fluids characteristics (current status of wettability, size of the reservoir, vertical continuity, fluid densities, viscosities, etc.)
 - Study the interplay between different forces under reservoir conditions (capillary, gravity, and viscous force)
 - Determine which properties to be changed (viscosity, density, wettability, etc.)
 - Screen wettability alteration methods based on the type reservoir rock type (sandstone, limestone, etc.) and the mechanism that had changed the reservoir's wettability
 - Optimize the parameters of wettability alteration
5. A new approach for enhance oil and oil recovery was presented. In this technique, both rock and fluid properties change by applying two stages :
 - Stage 1: Solvent is injected to change the oil properties such as density and viscosity.
 - Stage 2: Wettability alteration agent is injected to recover diluted oil (oil that is mixed with solvent). The selection of optimum type of wettability modifier depends on the rock and fluid properties.

6. Using this new approach, a broad range of wettability alteration agents was tested.
7. Solvent injection followed by wettability modifier injection was applied successfully to recover oil recovery in oil-wet systems that contain heavy oil/bitumen. Cationic surfactant type C12TAB, high pH solution using NaBO_2 , ionic liquid of BMMIM BF_4 , and zirconium nanoparticles can alter the wettability of heavy oil containing oil-wet carbonate reservoirs while anionic surfactants CS-330, high pH solution NaBO_2 , ionic liquid BMMIM BF_4 , and alumina nanofluid can alter the wettability of oil-wet sandstone (by aging them) reservoirs when they are injected after solvent treatment.
8. A new type of wettability alteration agent was presented. The solutions of imidazolium ionic liquids (BMIM BF_4 , BMMIM BF_4) at low concentrations (0.5-3.0 wt.%) were able to imbibe spontaneously into oil-wet sandstone and limestone yielding the best solvent retrieval among all other tested chemicals.
9. For optimizing oil recovery and solvent retrieval during hot-water phase of SOS-FR method, it was shown experimentally that:
 - Injection of water at moderate high temperature water is more efficient for oil recovery than high temperature, if enough time for imbibition is allowed. Wettability alteration may take place under this condition as the retrieved solvent will be replaced by the imbibing water.
 - Injection of water at high temperature (around the boiling point of the solvent), water is more efficient to solvent than high temperature if enough time is allowed.

Recommendations and Future Work

1. The solvent retrieval system developed here can be improved by including a cooling device such as spiral condenser or other cooling setups. To analyze the components of oil recovered during the solvent retrieval phase, the system can be connected to a gas chromatography instrument (GC).
2. Fluid displacement during solvent injection phase is governed by miscible flow in the micro channels. Visualization of this phenomenon using capillary tubes, Hele-Shaw, and micro models is recommended for better understanding of solvent /oil interaction in porous medium. Visualization methods can also be useful to identify and explain the contribution of different mechanisms of oil recovery and solvent retrieval during steam/hot-water phase.

3. Solvent retrieval is a complex process that involves 3 phases flowing simultaneously: Oil, solvent and water. Depending on the pressure and temperature of the system, these fluids can be in liquid or gaseous states. The optimization of different factors that affect this complicated process can be improved by integrating the experimental work that was performed in this study with analytical modeling and numerical simulation.
4. High pH solution NaBO_2 tested in this study showed a positive impact on oil recovery and solvent retrieval for all types of rock samples used (sandstone, limestone, and Grosmont cores). Clarification of the influence of this chemical on the wettability of NFCRs is essentially needed. The interest in the alkaline solution as wettability modifier in particular is ascribed to its relatively low cost.
5. Several nanofluids experimented during this investigation showed a tendency to alter the wettability of NFCRs. The partial instability of nanoparticles dispersion through the relatively long period of imbibition tests indicates that further research is needed to provide highly stable nanodispersions.
6. Imidazaolium ionic liquids tested in this study were efficiently successful in wettability alteration of oil-wet sandstone and limestone. The mechanisms of wettability alteration by this new type of chemicals are partially clarified in this work but were not fully investigated. In depth investigation into the interaction of Imidazaolium group with fluids (water, solvent, and oil) in porous medium (sandstone and carbonate) is of great importance.
7. Other groups of ionic liquids such ammonium and phosphonium may have similar potential to modify the wettability of porous medium from oil-wet to water-wet. It is therefore of interest to determine how these ionic liquid influence physiochemical characteristics of the matrix of the NFCRs.
8. The imbibition tests for most of the chemical solutions in this study were conducted under ambient temperature. It is recommended to explore the effect of temperature on the imbibition behaviour of wettability modifiers. The temperature range shall at least cover the temperatures encountered under reservoir conditions.
9. Up-scaling the results documented in this study is needed to assess the economical evaluation of this process. Key factors for this assessment would be cost of the chemicals, solvent retrieval, and oil recovery by wettability alteration. A prior optimization study to indicate the effect of several parameters such as solvent type and soaking period, wettability modifiers concentration, and fluids injection rate is highly recommended

References

Chapter 1:

1. Al-Bahlani, A.M. and Babadagli, T. 2008. Heavy-Oil Recovery in Naturally Fractured Reservoirs with Varying Wettability by Steam Solvent Co-Injection. Paper SPE 117626 presented at the SPE Int. Thermal Oper. and Heavy-Oil Symp., Calgary, AB, Canada, 20-23 October.
2. Al-Bahlani, A.M. and Babadagli, T. 2009a. Steam-Over-Solvent Injection in Fractured Reservoirs (SOS-FR) for Heavy-Oil Recovery: Experimental Analysis of the Mechanism. Paper SPE 123568 presented at the SPE Asia Pacific Oil and Gas Conference & Exhibition, Jakarta, Indonesia, 4-6 Aug.
3. Al-Bahlani, A.M. and Babadagli, T. 2009b. Laboratory and Field Scale Analysis of Steam-Over-Solvent Injection in Fractured Reservoirs (SOS-FR) for Heavy-Oil Recovery. Paper SPE 124047 presented at the SPE Annual Tech. Conf. and Exh., New Orleans, Louisiana, USA, 4-7 October.
4. Al-Bahlani, A.M. and Babadagli, T. 2010. Efficiency Analysis of Steam-Over-Solvent Injection in Fracture Reservoirs (SOS-FR) Method for Heavy-Oil Recovery. Paper SPE 132458 presented at the Western Reg. Meet., Anaheim, California, USA, 27-29 May.
5. Bobek, J. E., Mattax, C. C., and Denekas, M. O. 1958. Reservoir Rock Wettability-Its Significance and Evaluation. *Pet. Trans. AIME* 213: 155-160.
7. Giraldo, J., Benjumea, P., Lopera, S. et al. 2013. Wettability Alteration of Sandstone Cores by Alumina-Based Nanofluids. *Energy & Fuels* 27 (7): 3659-3665
8. Hatiboglu, C. U. and Babadagli, T. 2008. Primary and Secondary Oil Recovery from Different Wettability Rocks by Counter-Current Diffusion and Spontaneous Imbibition. *SPE Res. Eval. and Eng.* 11 (2): 418-428.
9. Karimi, A., Fakhroueian, Z., Bahramian, A. et al. 2012n. Wettability Alteration in Carbonates using Zirconium Oxide Nanofluids: EOR implications. *Energy & Fuels* 26 (2): 1028-1036.
10. Nasr, T.N., Beaulieu, G., Golbeck, H. 2003. Novel Expanding Solvent-SAGD Process "ES-SAGD". *J. Cdn. Pet. Tech* 42 (1): 13-16.
11. Rangriz-Shokri, A. and Babadagli, T. 2012a. Evaluation of Thermal/Solvent Applications with and without Cold Heavy Oil Production with Sand (CHOPS). Paper SPE 158934 presented at the 2012 SPE Energy Conference, Developing Resources for Sustainability, Port-of-Spain, Trinidad, 11-13 June.
12. Rangriz-Shokri, A. and Babadagli, T. 2012b. An Approach to Model CHOPS (Cold Heavy Oil Production with Sands) and Post-CHOPS Applications. Paper SPE 159437

presented at the 2012 SPE Annual Tech. Conf. and Exh., San Antonio, Texas, USA, 8-10 October.

13. Standnes, D.C. and Austad, T. 2000. Wettability alteration in chalk 2: Mechanism for Wettability Alteration From Oil-wet to Water-wet Using Surfactants. *J. Pet. Sci. Eng.* 28 (3): 123–143. doi: 10.1016/S0920-4105(00)00084-X.
14. Wagner, O.R. and Leach, R.O. 1959. Improving Oil Displacement Efficiency by Wettability Adjustment. SPE-1101-G. *Trans., AIME* 216: 65–72.

Chapter 2:

1. Al-Bahlani, A.M. and Babadagli, T. 2008. Heavy-Oil Recovery in Naturally Fractured Reservoirs with Varying Wettability by Steam Solvent Co-Injection. Paper SPE 117626 presented at the SPE Int. Thermal Oper. and Heavy-Oil Symp., Calgary, AB, Canada, 20-23 October.
2. Al-Bahlani, A.M. and Babadagli, T. 2009a. Steam-Over-Solvent Injection in Fractured Reservoirs (SOS-FR) for Heavy-Oil Recovery: Experimental Analysis of the Mechanism. Paper SPE 123568 presented at the SPE Asia Pacific Oil and Gas Conference & Exhibition, Jakarta, Indonesia, 4-6 Aug.
3. Al-Bahlani, A.M. and Babadagli, T. 2009b. Laboratory and Field Scale Analysis of Steam-Over-Solvent Injection in Fractured Reservoirs (SOS-FR) for Heavy-Oil Recovery. Paper SPE 124047 presented at the SPE Annual Tech. Conf. and Exh., New Orleans, Louisiana, USA, 4-7 October.
4. Al-Bahlani, A.M. and Babadagli, T. 2010. Efficiency Analysis of Steam-Over-Solvent Injection in Fractured Reservoirs (SOS-FR) Method for Heavy-Oil Recovery. Paper SPE 132458 presented at the Western Reg. Meet., Anaheim, California, USA, 27-29 May.
5. Al-Gosayir, M., Babadagli, T. and Leung, J. 2013. Design of SOS-FR (Steam-Over-Solvent Injection in Fractured Reservoirs) Method for Heavy-Oil Recovery Using Hybrid Optimization Frame work. Paper SPE 164306 presented at 18th Middle East Oil and Gas Show and Conference (MEOS), Manama, Bahrain, 10-13 March.
6. Arciniegas, L. and Babadagli, T. 2013. Optimal Application Conditions of Solvent Injection into Oilsands to Minimize the Effect of Asphaltene Deposition: An Experimental Investigation. Paper SPE 165531 submitted to the 2013 SPE Heavy Oil Conf., Calgary, Alberta, Canada, 11-13 June.
7. Coskuner, G., Naderi, K. and Babadagli, T. 2013. An Enhanced Oil Recovery Technology as a Follow Up to Cold Heavy Oil Production with Sand. Paper SPE 165385 presented at the 2013 SPE Heavy Oil Conf., Calgary, AB, Canada, 11-13 June.

8. Dehghan, A.A., Farzaneh, S.A., Kharrat, R., Ghazanfari, M.H. 2009. The role of pore geometry and connate water miscible displacement of heavy oil with hydrocarbon solvents in strongly water-wet and oil-wet media using five-spot micromodels. Presented at Canadian international petroleum conference, Calgary, Alberta, Canada, 16–18 June.
9. Joseph, D. D. 1990. Fluid Dynamics of Two Miscible Fluids with Diffusion and Gradient Stresses," *Eur. J. Mech., B/Fluids*, **9**, 565-596.
10. Korteweg, D. 1901 Sur la forme que prennent les équations du mouvement des fluides si l'on tient compte des forces capillaires causées par des variations de densité. *Arch. Néerl. Sciences Exactes et Naturelles, Series II*, **6**, 1–24.
11. Li, W., Mamora, D.D. and Li, Y. 2011a. Light-and Heavy-Solvent Impacts on Solvent-Aided-SAGD Process: A Low-Pressure Experimental Study. *J. Cdn. Pet. Tech* **50** (4): 19-30.
12. Li, W., Mamora, D.D. and Li, Y. 2011b. Solvent-Type and -Ratio Impacts on Solvent-Aided SAGD Process. *SPE Res Eval and Eng.* **14** (3): 320-331.
13. Maini, B., Ionescu, E. and Batycky, J. 1986. Miscible Displacement of Residual Oil – Effect of Wettability on Dispersion in Porous Media. *JCPT*, May-June, Montreal, 36-41.
14. Naderi, K. and Babadagli, T. 2012. Experimental Analysis of Heavy Oil Recovery and CO₂ Storage by Alternate Injection of Steam and CO₂ in Deep Naturally Fractured Reservoir. Paper SPE 146738 presented at the 2012 Heavy Oil Conference Canada, Calgary, Alberta, Canada 12-14 June.
15. Naderi, K., Babadagli, T. and Coskuner, G. 2013. Bitumen Recovery by the SOS-FR (Steam-Over-Solvent Injection in Fractured Reservoirs) Method: An Experimental Study on Grosmont Carbonates. Paper SPE 165530 submitted to the 2013 SPE Heavy Oil Conf., Calgary, Alberta, Canada, 11-13 June.
16. Nasr, T.N., Beaulieu, G., Golbeck, H. 2003. Novel Expanding Solvent-SAGD Process “ES-SAGD” *J. Cdn. Pet. Tech* **42** (1): 13-16.
17. Pojman, J. A.; Whitmore, C.; Turco Liveri, M. L.; Lombardo, R.; Marszalek, J.; Parker, R.; Zoltowski, B. "Evidence for the Existence of an Effective Interfacial Tension between Miscible Fluids: Isobutyric Acid-Water and 1-Butanol-Water in a Spinning-Drop Tensiometer," *Langmuir* 2006, **22**, 2569-2577.
18. Rangriz-Shokri, A. and Babadagli, T. 2012a. Evaluation of Thermal/Solvent Applications with and without Cold Heavy Oil Production with Sand (CHOPS). Paper SPE 158934 presented at the 2012 SPE Energy Conference, Developing Resources for Sustainability, Port-of-Spain, Trinidad, 11-13 June.
19. Rangriz-Shokri, A. and Babadagli, T. 2012b. An Approach to Model CHOPS (Cold Heavy Oil Production with Sands) and Post-CHOPS Applications. Paper SPE 159437

presented at the 2012 SPE Annual Tech. Conf. and Exh., San Antonio, Texas, USA, 8-10 October.

20. Rezaei, N., Mohammadzadeh, O., Parsaei, R., Chatzis, I. 2010. The effect of reservoir wettability on the production characteristics of the VAPEX process. Paper SPE 130096, presented at the SPE Improved Oil Recovery Symposium, Tulsa, 24–28 April.

Chapter 3:

1. Abdallah, W., Buckley, J.S., Carnegie, A., et al. 2007. Fundamentals of Wettability. *Oilfield Rev.* 19 (2): 44–61.
2. Adibhatla, B. and Mohanty, K.K. 2008. Oil Recovery From Fractured Carbonates by Surfactant-Aided Gravity Drainage: Laboratory Experiments and Mechanistic Simulations. *SPE Res Eval & Eng* 11 (1): 119–130. SPE-99773-PA. doi: 10.2118/99773-PA.
3. Afrapoli, M. S., Crescente, C., Alipour, S., et al. 2009. The Effect of Bacterial Solution on the Wettability index and Residual Oil Saturation in Sandstone. *J. Petr. Sci. and Eng* 69, (3):, 255-260.
4. ALawati, S. and Saleh, S. 1996. Oil Recovery in Fractured Oil Reservoirs by Low IFT Imbibition Process. Paper SPE 36688 presented at the SPE Annual Technical Conference and Exhibition, Denver, 6–9 October.
5. Al-Bahlani, A.M. and Babadagli, T. 2008. Heavy-Oil Recovery in Naturally Fractured Reservoirs with Varying Wettability by Steam Solvent Co-Injection. Paper SPE 117626 presented at the SPE Int. Thermal Oper. and Heavy-Oil Symp., Calgary, AB, Canada, 20-23 October.
6. Al-Hadhrami, H.S. and Blunt, M.J. 2000. Thermally Induced Wettability Alteration to Improve Oil Recovery in Fractured Reservoirs. Paper SPE 59289 presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, 3–5 April. doi: 10.2118/59289-MS.
7. Alvarez, J. O., Neog, A., Jais, A., & Schechter, D. S. 2014. Impact of Surfactants for Wettability Alteration in Stimulation Fluids and the Potential for Surfactant EOR in Unconventional Liquid Reservoirs. Paper SPE 169001 presented at the SPE Unconventional Resources Conference, Texas, USA, 1-3 April. <http://dx.doi.org/10.2118/169001-MS>.
8. Alveskog, P.L., Holt, T., and Torsæter, O. 1998. The Effect of Surfactant Concentration on the Amott Wettability Index and Residual Oil Saturation. *J. Petr. Sci. Eng.* 20 (3–4): 247–252. [http://dx.doi.org/10.1016/S0920-4105\(98\)00027-8](http://dx.doi.org/10.1016/S0920-4105(98)00027-8).
9. Alotaibi, M.B., Nasralla, R.A., and Nasr-El-Din, H.A. 2010. Wettability Studies Using Low-Salinity Water in Sandstone Reservoirs. Paper OTC 20718 presented at the Offshore Technology Conference, Houston, USA, 3–6 May.

10. Anderson, W.G. 1986. Wettability Literature Survey—Part I: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability. *JPT* 38 (10): 1125–1144. SPE-13932-PA. DOI: 10.2118/13932-PA.
11. Armand, M., Endres, F., MacFarlane, D. R. et al. 2009. Ionic-liquid Materials for the Electrochemical Challenges of the Future. *Nature Materials* 8 (8): 621–629.
12. Austad, T. and Milner, J. 1997. Spontaneous Imbibition of Water into Low Permeable Chalk at Different Wettabilities Using Surfactants. Paper SPE 37236 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 18–21 February. doi: 10.2118/37236-MS
13. Austad, T. and Standnes, D.C. 2003. Spontaneous Imbibition of Water into Oil-Wet Carbonates. *J. Pet. Sci. Eng.* 39 (3–4): 363–376. [http://dx.doi.org/10.1016/S0920-4105\(03\)00075-5](http://dx.doi.org/10.1016/S0920-4105(03)00075-5).
14. Austad, T., Strand, S., Høgenesen, E.J., and Zhang, P. 2005. Seawater as IOR Fluid in Fractured Chalk. Paper SPE 93000 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 2–5 February. doi: 10.2118/93000-MS.
15. Babadagli, T. 1996. Temperature Effect on Heavy-Oil Recovery by Imbibition in Fractured Reservoirs. *J. Petr. Sci. and Eng* 14 (3): 197–208.
16. Babadagli, T. 2001. Scaling of Co-current and Counter-Current Capillary Imbibition for Surfactant and Polymer Injection in Naturally Fractured Reservoirs. *SPE J.* 6 (4): 465–478. SPE-74702-PA. doi: 10.2118/74702-PA.
17. Babadagli, T. 2002. Dynamics of Capillary Imbibition when Surfactant, Polymer, and Hot Water are used as aqueous phase for oil recovery. *J. Colloid Interface Sci* 246 (1): 203–213.
18. Babadagli, T. 2003. Analysis of Oil Recovery by Spontaneous Imbibition of Surfactant Solution. Paper SPE 84866 presented at SPE International Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur, Malaysia, 20–21 October.
19. Babadagli, T., Al-Bemani, A., and Boukadi, F. 1999. Analysis of Capillary Imbibition Recovery Considering the Simultaneous Effects of Gravity, Low Ift, and Boundary Conditions. Paper presented at the SPE Asia Pacific Improved Oil Recovery Conference, Kuala Lumpur, Malaysia, 25–26 October. doi:10.2118/57321-ms.
20. Benzagouta, M. S., AlNashef, I. M., Karnanda, W. and Al-Khidir, K. 2013. Ionic liquids as Novel Surfactants for Potential Use in Enhanced Oil Recovery. *Korean J. Chem. Eng.* 30 (11): 2108–2117.
21. Berg, S., Cense, A.W., Jansen, E., and Bakker, K. 2009. Direct Experimental Evidence of Wettability Modification by Low Salinity. Paper SCA 2009-12 presented at the 23rd International Symposium of the Society of Core Analysts, Noordwijk aan Zee, The Netherlands, 27–30 September.

22. Bobek, J. E., Mattax, C. C., and Denekas, M. O. 1958. Reservoir Rock Wettability-Its Significance and Evaluation. *Pet. Trans. AIME* 213: 155-160.
23. Buckley, J.S., Takamura, K., and Morrow, N.R. 1989. Influence of Electric Surface Charges on the Wetting Properties of Crude Oils. *SPE Res Eng* 4 (3): 332–340. SPE-16964-PA. doi: 10.2118/16964-PA.
24. Buckley, J. S. and Liu, Y. 1998. Some mechanisms of crude oil/brine/solid interactions. *J. Pet. Sci. Eng.* 20 (3): 155-160.
25. Chen, H.L., Lucas, L.R., Nogaret, L.A.D, Yang, H.D., and Kenyon, D.E. 2000. Laboratory Monitoring of Surfactant Imbibition Using Computerized Tomography. Paper SPE 59006 presented at the SPE/DOE International Petroleum Conference and Exhibition in Mexico, Villahermosa, Mexico, 1–3 February. doi: 10.2118/59006-MS.salehi.
26. Chilingar, G.V. and Yen, T.F. 1983. Some Notes on Wettability and Relative Permeability of Carbonate Rocks. *Energy Sources* 7 (1): 67–75.
27. Dakik, A. and Gupta, A. 2013. Improvement of Waterflood Oil Recovery by Wettability Alteration in Carbonate Reservoirs. In Proceedings of the ASME 2013 32nd International Conference on Ocean, Offshore and Arctic Engineering, Nantes, France, 9-14 June.
28. Denekas, M. O., Mattax, C. C. and Davis, G. T. 1959. Effects of crude oil components on rock wettability. *Pet. Trans. AIME* 216: 330-333.
29. Dyson, P. J. and Geldbach, T. J. 2007. Applications of ionic liquids in synthesis and catalysis. *Interface-Electrochemical Society* 16 (1): 50-53.
30. Ehrlich, R. and Wygal, R.J. 1977. Interrelation of Crude Oil and Rock Properties with the Recovery of Oil by Caustic Waterflooding. *SPE J.* 17 (4): 263–270. doi: 10.2118/5830-PA.
31. Feng, L., Li, S., Li, Y., et al. 2002. Super-Hydrophobic Surfaces: From Natural to Artificial. *Advanced materials* 14 (24): 1857-1860.
32. Giraldo, J., Benjumea, P., Lopera, S. et al. 2013. Wettability Alteration of Sandstone Cores by Alumina-Based Nanofluids. *Energy & Fuels* 27 (7): 3659-3665.
33. Golabi E., Azad F.S., Ayatollahi S.S., Hosseini S.N., et al. 2012. Experimental Study of Anionic and cationic Surfactants Effects on Reduce of IFT and Wettability Alteration in Carbonate Rock. *Int J Sci Eng Res* 3 (7): 1-8.
34. Golabi E., Azad F.S., and Ayatollahi, S.S. 2009. Chemical Induced Wettability Alteration of Carbonate Reservoir Rocks. *Int J Sci Eng Res* 6 (1): 66-73.
35. Gupta, R. and Mohanty, K.K. 2008. Wettability Alteration of Fractured Carbonate Reservoirs. Paper SPE 113407 presented at SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, 20–23 April. doi:10.2118/113407-MS.
36. Gupta, R. and Mohanty, K. 2010. Temperature Effects on Surfactant-Aided Imbibition

- into Fractured Carbonates. *SPE J.* 15 (3): 588-597. doi: 10.2118/110204-PA.
37. Gupta, R. and Mohanty, K. K. 2011. Wettability Alteration Mechanism For Oil Recovery From Fractured Carbonate Rocks. *Transport in porous media* 87 (2): 635-652.
 38. Hamouda, A.A. and Gomari, K.A.R. 2006. Influence of Temperature on Wettability Alteration of Carbonate Reservoirs. Paper SPE 99848 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 22–26 April. doi: 10.2118/99848-MS.
 39. Hendraningrat L., Li S., Torsæter O., 2013. Effect of Some Parameters Influencing Enhanced Oil Recovery Process Using Silica Nanoparticles: An experimental investigation. Paper SPE-165955 presented at SPE Reservoir Characterisation and Simulation Conference and Exhibition, Abu Dhabi, UAE, 16–18 September.
 40. Hirasaki, G. and Zhang, D.L. 2004. Surface Chemistry of Oil Recovery from Fractured, Oil-Wet, Carbonate Formation. *SPE J.* 9 (2): 151–162. doi:<http://dx.doi.org/10.2118/110204-PA>.
 41. Høgnesen, E.J., Olsen, M., and Austad, T. 2006. Capillary and Gravity Dominated Flow Regimes in Displacement of Oil from an Oil-Wet Chalk Using Cationic Surfactant. *Energy Fuels* 20 (3): 1118–1122. doi: 10.1021/ef050297s.
 42. Hogshead, C. G., Manias, E., Williams, P., Lupinsky, A. and Painter, P. 2010. Studies of bitumen– silica and oil– silica interactions in ionic liquids. *Energy & Fuels* 25 (1): 293-299.
 43. Hu, Y. F. and Guo, T. M. 2005. Effect of the Structures of Ionic Liquids and Alkylbenzene-Derived Amphiphiles on the Inhibition of Asphaltene Precipitation From CO₂-Injected Reservoir Oils. *Langmuir* 21 (18): 8168-8174.
 44. Jadhunandan, P.P. and Morrow, N.R. 1991. Effect of Wettability on Waterflood Recovery for Crude Oil/Brine/Rock Systems. Paper SPE 22597 prepared for presentation at the 66th Annual Technical Conference and Exhibition, Dallas, TX, 6 – 9 October.
 45. Joonaki, E., Ghanaatian, S.H. and Zargar, G.H. 2012. A New Approach to Simultaneously Enhancing Heavy Oil Recovery and Hindering Asphaltene Precipitation. *Iranian Journal of Oil and Gas Science and Technology* 1: 37-42.
 46. José-Alberto, M. H. and Jorge, A. 2011. Current Knowledge and Potential Applications of Ionic Liquids in the Petroleum Industry. *Ionic liquids: Applications and Perspectives, In Tech*: 439-456.
 47. Ju, B. and Fan, T. 2009. Experimental study and mathematical model of nanoparticle transport in porous media. *Powder Technology* 192 (2): 195-202.
 48. Ju, B., Fan, T. and Li, Z. 2012. Improving Water Injectivity and Enhancing Oil Recovery by Wettability Control Using Nanopowders. *J. Petr. Sci. and Eng* 86: 206-216. doi: 10.1016/j.petrol.2012.03.022.
 49. Karimi, A., Fakhroueian, Z., Bahramian, A. et al. 2012n. Wettability Alteration in

- Carbonates using Zirconium Oxide Nanofluids: EOR implications. *Energy & Fuels* 26 (2): 1028-1036.
50. Karimi, M., Mahmoodi, M., Niazi, A. et al. 2012b. Investigating Wettability Alteration During MEOR Process, A micro/Macro Scale Analysis. *Colloids and Surfaces B: Biointerfaces* 95: 129-136.
 51. Kowalewski, E., Rueslåtten, I., Steen, K.H., et al. 2006. Microbial Improved Oil Recovery—Bacterial Induced Wettability and Interfacial Tension Effects on Oil Production. *J. Petr. Sci. and Eng* 52 (1): 275-286.
 52. Leach, R. O., Wagner, O. R., Wood, H.W., et al. 1962. A laboratory and field study of wettability adjustment in water flooding. *JPT* 14 (02): 206-212.
 53. Li, K. and Firoozabadi, A. 2000. Experimental Study of Wettability Alteration to Preferentially Gas-Wetting in Porous Media and Its Effects. *SPE REE* 3 (2): 139–149. doi: 10.2118/62515-PA.
 54. Liu, W., Zhao, T., Zhang, Y., Wang, H., et al. 2006b. The Physical Properties of Aqueous Solutions of the Ionic Liquid [BMIM][BF₄]. *J. Solution Chem.* 35 (10): 1337-1346.
 55. Liu, Q., Dong, M., and Ma, S. 2006. Alkaline/Surfactant Flood Potential in Western Canadian Heavy Oil Reservoirs. Paper SPE 99791 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 22–26April.
 56. Lo, W. H., Yang, H. Y. and Wei, G. T. 2003. One-spot Desulfurization of Light Oils by Chemical Oxidation and Solvent Extraction with Room Temperature Ionic Liquids. *Green Chemistry* 5 (5): 639-642.
 57. Maghzi, A., Mohammadi, S., Ghazanfari, M. H. et al. 2012a. Monitoring Wettability Alteration by Silica Nanoparticles During Water Flooding to Heavy Oils in Five-Spot Systems: A Pore-Level Investigation. *Experimental Thermal and Fluid Science* 40: 168-176. <http://dx.doi.org/10.1016/j.expthermflusci.2012.03.004>.
 58. Malham, I.B., Letellier, P. and Turmine, M. 2006. Evidence of A Phase Transition in Water-1-butyl-3-methylimidazolium tetrafluoroborate and Water-1-butyl-2, 3-dimethylimidazolium tetrafluoroborate mixtures at 298 K: Determination of the Surface Thermal Coefficient, b T, P. *J. Phys. Chem. B* 110 (29): 14212-14214.
 59. McElfresh, P., Holcomb, D., Ector, D. 2012. Application of Nanofluid Technology to Improve Recovery in Oil and Gas Wells. Paper SPE 154827 presented at the SPE International Oilfield nanotechnology Conference, Noordwijk, The Netherland, 12-14June.
 60. Mohammed, M. and Babadagli, T. 2014a. Alteration of Matrix Wettability During Alternate Injection of Hot-water/Solvent into Heavy-oil Containing Fractured Reservoirs. Paper SPE 170034 presented at the SPE Heavy-Oil Conference, Calgary, Alberta, Canada, 10–12 June. <http://dx.doi.org/10.2118/170034-MS>

61. Mohammed, M. and Babadagli, T. 2014b. Alteration of Matrix Wettability During Alternate Injection of Hot-water/Solvent into Heavy-oil Containing Fractured Reservoirs. Submitted to *SPE Res. Eval. and Eng.* for publication.
62. Morrow, N.R. 1975. The Effects of Surface Roughness on Contact Angle with Special Reference to Petroleum recovery. *J. Can. Pet. Tech.* 14: 42–54.
63. Morrow, N.R. 1990. Wettability and Its Effect on Oil Recovery. *J Pet Technol* 24 (12): 1476–1484. SPE-21621-PA. doi: 10.2118/21621-PA.
64. Morrow, N. and Buckley, J.2011. Improved Oil Recovery by Low-Salinity Waterflooding. *JPT* 63 (05):106-112.
65. Morsy, S. and Sheng, J. J. 2014. Paper SPE 168984 presented in SPE Unconventional Resources Conference, Texas, USA, 1-3 April. <http://dx.doi.org/10.2118/168984-MS>
66. Najafabadi, N.F., Delshad, M., Sepehrnoori, K., Nguyen, Q.P., and Zhang, J. 2008. Chemical Flooding of Fractured Carbonates Using Wettability Modifiers. Paper SPE 113369 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 20–23 April. doi: 10.2118/113369-MS.
67. Morrow, N.R. and Mason, G. 2001. Recovery of Oil by Spontaneous Imbibition. *Current Opinion in Colloid & Interface Science* 6 (4): 321–337. doi: 10.1016/S1359-0294(01)00100-5.
68. Nasralla, R.A., Bataweel, M.A. and Nasr-El-Din, H.A. 2013. Investigation of Wettability Alteration and Oil Recovery Improvement by Low-Salinity Water in Sandstone Rock. *JPT* 52 (2):144–154.
69. Nasralla, R.A. and Nasr-El-Din, H.A. 2014. Double-Layer Expansion: Is It a Primary Mechanism of Improved Oil Recovery by Low-Salinity Waterflooding? *SPE Res Eval & Eng* 17 (1): 49–59. SPE-154334-PA. <http://dx.doi.org/10.2118/154334-PA>.
70. Onyekonwu, M. and Ologo, N. 2010. Investigating in Use of Nanoparticles in Enhancing Oil Recovery. Paper SPE 140744 presented at 34th Annual SPE International Conference and Exhibition held in Tinapa – Calabar. Tinapa – Calabar, 31- August 7 Nigeria, July.
71. Ogolo N.A., Olafuyi O.A. and Onyekonwu M.O. 2012. Enhanced Oil Recovery Using Nanoparticles. Paper SPE 160847 presented at the SPE Saudi Arabia section technical symposium and exhibition, Al-Khobar, Saudi Arabia, 8–11 April.
72. Painter, P., Williams, P. and Lupinsky, A. 2010. Recovery of Bitumen From Utah Tar Sands Using Ionic Liquids. *Energy & Fuels* 24 (9): 5081-5088.
73. Painter, P., Williams, P. and Mannebach, E. 2009. Recovery of Bitumen From Oil or Tar sands using ionic liquids. *Energy & Fuels* 24 (2): 1094-1098.
74. Pons-Jiménez M., Cartas-Rosado R., Martínez-Magadán José-Manuel et al. 2014. Theoretical and Experimental Insights on the True Impact of C12TAC Cationic Surfactant in Enhanced Oil Recovery for Heavy Oil Carbonate Reservoirs. *Colloids Surf*

A. 455: 76–91

75. Rao, D. N. 1999. Wettability Effects in Thermal Recovery Operations. *SPE Reservoir Evaluation & Engineering* 2(05): 420-430.
76. RezaeiDoust, A., Puntervold, T., Strand, S. et al. 2009. Smart Water as Wettability modifier in Carbonate and Sandstone: A Discussion of Similarities/Differences In the chemical mechanisms. *Energy & Fuels* 23 (9): 4479-4485.
77. Rogers, R. D. and Seddon, K. R. 2003. Ionic Liquids--Solvents of the Future? *Science* 302 (5646): 792-793.
78. Sakuma, H., Andersson, M. P., Bechgaard, K. et al. 2014. Surface Tension Alteration on Calcite, Induced by Ion Substitution. *J. Phys. Chem. C* 118 (6): 3078-3087
79. Salathiel, R. A. 1973. Oil Recovery by Surface Film Drainage in Mixed-Wettability Rocks. *J. Pet. Technol.* 25: 1216–1224. <http://dx.doi.org/10.2118/4104-PA>.
80. Safari, M. E. H. D. I. and Jamialahmadi, M. 2013. Effect of Polysilicon Nanoparticles on Enhanced Oil Recovery in Iranian Oil Reservoir. *Int. J. Nano Dimens* 3 (3): 199-205.
81. Saleh, T.S. and Graves, R.M.Y., 1993. Experimental Investigation of Linear Scaling of Micellar Displacement in Porous Media. SPE paper 251, 72, 2-5 March.
82. Salehi, M., Johnson, S. J., and Liang, J. T. 2008. Mechanistic Study of wettability Siteration Ssing Surfactants with Splications in Saturally Sractured Seservoirs. *Langmuir* 24 (24): 14099-14107.
83. Schechter, D.S., Zhou, D., and Orr, F.M. Jr. 1991. Capillary Imbibition and Gravity Segregation in Low IFT Systems. Paper SPE 22594 presented at the SPE Annual Technical Conference and Exhibition, Dallas, 6–9 October.
84. Schechter, D.S., Zhou, D., and Orr, F.M. Jr. 1994. Low IFT drainage and imbibition. *J. Pet. Sci. Eng.* 11 (4): 283–300. doi: 10.1016/0920-4105(94)90047-7.
85. Schembre, J.M., Tang, G.-Q., and Kovscek, A.R. 2006. Interrelationship of Temperature and Wettability on the Relative Permeability of Heavy Oil in Diatomaceous Rocks. *SPE Res Eval & Eng* 9 (3): 239–250. SPE-93831-PA. doi: 10.2118/93831-PA.
86. Seethepalli, A. Adibhatla, B., and Mohanty, K.K. 2004. Physico-Chemical Interactions During Surfactant Flooding of Fractured Carbonate Reservoirs. *SPE J.* 9 (4): 411–418. SPE-89423-PA. doi: 10.2118/89423-PA.
87. Sharma, G., and Mohanty, K. K. 2011. Wettability Alteration in High Temperature and High Salinity Carbonate Reservoirs. Paper SPE 147306 presented at SPE ATCE, Denver, CO, 30 October-2 November.
88. Shokrlu Y.H., Babadagli T. 2010. Effects of Nano-Sized Metals on Viscosity Reduction of Heavy oil/Bitumen During Thermal Tpplications. Paper CSUG/SPE 137540 presented at the Canadian Unconventional Resources and International Petroleum Conference, Calgary, Canada, 19–21October.

89. Hamed Shokrlu, Y. and Babadagli, T. 2014. Kinetics of the In-Situ Upgrading of Heavy Oil by Nickel Nanoparticle Catalysts and Its Effect on Cyclic-Steam-Stimulation Recovery Factor. *SPE Res Eval & Eng* 17 (3): 355-364. <http://dx.doi.org/10.2118/170250-PA>
90. Solga, A., Cerman, Z., Striffler, B. F., Spaeth, M. et al. 2007. The Dream of Staying Clean: Lotus and Biomimetic Surfaces. *Bioinspiration & Biomimetics* 2 (4): 126-134. doi:10.1088/1748-3182/2/4/S02.
91. Spinler, E.A. and Baldwin, B.A. 2000. Surfactant Induced Wettability Alteration in Porous Media. In *Surfactants: Fundamentals and Applications in the Petroleum Industry*, ed. L.L. Schramm, 159–202. Cambridge, UK: Cambridge University Press.
92. Standnes, D.C. and Austad, T. 2000. Wettability alteration in chalk 2: Mechanism for Wettability Alteration From Oil-wet to Water-wet Using Surfactants. *J. Pet. Sci. Eng.* 28 (3): 123–143. doi: 10.1016/S0920-4105(00)00084-X.
93. Standnes, D.C. and Austad, T. 2003a. Wettability Alteration in Carbonates: Interaction Between Cationic-Surfactant and Carboxylates as a KeyFactor in Wettability Alteration From Oil-Wet to Water-Wet Conditions. *Colloids Surf. A Physicochem. Eng. Asp.* 216 (1–3): 243–259. [http://dx.doi.org/10.1016/S0927-7757\(02\)00580-0](http://dx.doi.org/10.1016/S0927-7757(02)00580-0).
94. Standnes, D.C. and Austad, T. 2003b. Nontoxic Low-Cost Amines as WettabilityAlteration Chemicals in Carbonates. *J. Petroleum Science and Engineering* 39 (3–4): 431–446. doi: 10.1016/S0920-4105(03)00081-0.
95. Stoll, W.M., Hofman, J.P., Ligtheim, D.J. et al. 2008. Toward Field-Scale Wettability Modification—The Limitation of Diffusive Transport. *SPE Res Eval & Eng* 11 (3): 633–640. SPE-107095-PA. doi: 10.2118/107095-PA.
96. Strand, S., Høghensen, E.J., and Austad, T. 2006. Wettability Alteration of Carbonates; Effect of Potential Determining Ions (Ca^{+2} , SO_4^{-2}) and Temperature. *Colloids Surf. A Physicochem. Eng. Asp.* 275 (1–3): 1–10. <http://dx.doi.org/10.1016/j.colsurfa.2005.10.061>.
97. Strand, S., Standnes, D.C., and Austad, T. 2003. Spontaneous Imbibition of Aqueous Surfactant Solution into Neutral to Oil-Wet Carbonate Cores: Effects of Brine Salinity and Composition. *Energy and Fuels* 17 (5): 1133–1144. DOI: 10.1021/ef030051s.
98. Strand, S., Puntervolt, T., and Austad, T. 2008. Effect of Temperature on Enhanced Oil Recovery from Mixed-Wet Chalk Cores by SpontaneousImbibition and Forced Displacement Using Seawater. *Energy Fuels* 22 (5): 3222–3225. <http://dx.doi.org/10.1021/ef800244v>.
99. Strand, S., Austad, T., Puntervold, T. et al .2008. “Smart Water” for Oil Recovery from Fractured Limestone: A Preliminary Study. *Energy & Fuels* 22: 3126–3133.
100. Tabataba, A Gonzalez, M.V., Harwell, J.H., and Scamehorn, J.F. 1993. Reducing

- Surfactant Adsorption in Carbonate Reservoirs. *SPE Res Eng* 8 (2): 117–122. SPE-24105-PA. doi: 10.2118/24105-PA.
101. Takahashi, S., and Kovscek, A. R., 2010a. Spontaneous Countercurrent Imbibition and Forced Displacement Characteristics of Low-Permeability, Siliceous Shale Rocks. *J. Petr. Sci. and Eng* 71 (1): 47-55.
102. Takahashi, S. and Kovscek, A. R. 2010b. Wettability Estimation of Low-Permeability, Siliceous Shale Using Surface Forces. *J. Petr. Sci. and Eng* 75 (1): 33-43.
103. Tang, G.Q. and Morrow, N.R. 1997. Salinity Temperature, Oil Composition, and Oil Recovery by Waterflooding. *SPE Reservoir Engineering* 12 (4): 269-276.
104. Tang, G. Q. and Morrow, N. R. 1999. Influence of Brine Composition and Fines Migration on Crude oil/Brine/Rock Interactions and Oil Recovery. *J. Petr. Sci. and Eng* 24 (2): 99-111.
105. Vafaei, S., Borca-Tasciuc, T., Podowski, M. Z et al. 2006. Effect of Nanoparticles on Sessile Droplet Contact Angle. *Nanotechnology* 17 (10): 2523-2527. doi:10.1088/0957-4484/17/10/014.
106. Vijapurapu, C.S. and Rao, D.N. 2004. Compositional Effects of Fluids on Spreading, Adhesion and Wettability in Porous Media. *Colloids & Surface A: Physicochem. Eng. Aspects* 241 (1–3): 335–342. DOI:10.1016/j.colsurfa.2004.04.024.
107. Vledder, P., Fonseca, J.C., Wells, T., et al. 2010. Low Salinity Water Flooding: Proof Of Wettability Alteration On A Field Wide Scale. Paper SPE129564 presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 24–28 April.
108. Wamkam, C. T., Opoku, M. K., Hong, H. et al. 2011. Effects of pH on Heat Transfer Nanofluids Containing ZrO₂ and TiO₂ nanoparticles. *J. Appl. Phys.* 109. <http://dx.doi.org/10.1063/1.3532003>
109. Wang, Y., Xu, H., Yu, W., Bai, B., Song, X. and Zhang, J. 2011. Surfactant Induced Reservoir Wettability Alteration: Recent Theoretical and Experimental Advances in Enhanced Oil Recovery. *Petroleum Science* 8 (4): 463-476.
110. Wagner, O.R. and Leach, R.O. 1959. Improving Oil Displacement Efficiency by Wettability Adjustment. SPE-1101-G. *Trans., AIME* 216: 65–72.
111. Wasan, D.T. and Nikolov, A.D. 2003. Spreading of Nanofluids on Solids. *Nature* 423.
112. W. C. Williams, I. C. Bang, E. Forrest et al. 2006. Preparation and Characterization of Various Nanofluids. In Proceedings of the NSTI Nanotechnology Conference and Trade Show (Nanotech '06) 2: 408–411.
113. Wasserscheid, P. and Keim, W. 2000. Ionic Liquids-New " Solutions" for Transition Metal Catalysis. *Angewandte Chemie* 39 (21): 3772-3789.
114. Wei, Q.F., Wang, X.Q., Mather, R.R. and Fotheringham, A.F. 2003. ESEM Study of Size Removal from Ceramic Fibers by Plasma Treatment. *Appl. Surf. Sci.* 220 (2003):217-223.

doi:10.1016/S0169-4332(03)00867-5.

115. Wickramathilaka, S., Morrow, N.R., and Howard J. 2010. Effect of Salinity on Oil Recovery by Spontaneous Imbibition. Paper SCA 2010-12 presented at the 24th International Symposium of Core Analysts, Halifax, Canada, 4–7. Oct.
116. Williams, P., Lupinsky, A. and Painter, P. 2010. Recovery of Bitumen From Low-Grade oil Sands Using Ionic Liquids. *Energy & Fuels* 24 (3): 2172-2173.
117. Winsor, P.A. 1954. Solvent Properties of Amphiphilic Compounds. London: Butterworth's Scientific Publications.
118. Wu, Y., Shuler, P. J., Blanco, M., Tang, Y., and Goddard, W. A. 2008. An experimental Study of Wetting Behavior and Surfactant EOR in Carbonates with Model Compounds. *SPE J.* 13 (01): 26-34. <http://dx.doi.org/10.2118/99612-PA>.
119. Xie, Q., He S. L. and Pu W. F. 2010. The Effects of Temperature and Acid Number of Crude Oil on the Wettability of Acid Volcanic Reservoir Rock From the Hailar Oil field. *Petroleum Science* 7 (1): 93-99.
120. Xie, X., Weiss, W.W., Tong, Z. et al. 2004. Improved Oil Recovery From Carbonate Reservoirs by Chemical Stimulation. Paper SPE 89424, Proc. of the Symposium on Improved Oil Recovery, Tulsa, 17–21 April. <http://dx.doi.org/10.2118/89424-MS>.
121. Yousef, A.A., Al-Saleh, S.H., and Al-Jawfi, M.S. 2011. New Recovery Method for Carbonate Reservoirs through Tuning the Injection Water Salinity: Smart Water Flooding. Paper SPE 143550 presented at the SPE EUROPEC/EAGE Conference and Exhibition, Vienna, Austria, 23–26 May.
122. Yousef, A. A., Liu, J., Blanchard, G. et al. 2012. Smart Water Flooding: Industry's First Field Test in Carbonate Reservoirs. Paper SPE 159526 presented at the SPE Annual Technical Conference and Exhibition, Texas, 8-10 Oct.
123. Yu W., Xie H. 2012. A Review on Nanofluids: Preparation, Stability Mechanisms and Applications. *J Nanomater* 2012: 1–17. doi:10.1155/2012/435873.
124. Yuan Y. H. and Lee T. R. 2013. Contact Angle and Wetting Properties. In *Surface Science Techniques*, Bracco G, Holst B eds., Chap. 1, 3–34, New York City, USA, Springer.
125. Zhang, D.L., Liu, S., Puerto, M., Miller, C.A., and Hirasaki, G.J. 2006. Wettability Alteration and Spontaneous Imbibition in Oil-Wet Carbonate Formations. *Journal of Petroleum Science and Engineering* 52 (1–4): 213–226. doi: 10.1016/j.petrol.2006.03.009.
126. Zhang, P. and Austad, T. 2005. The Relative Effects of Acid Number and Temperature on Chalk Wettability. Paper SPE 92999 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 2–4 February. doi: 10.2118/92999-MS.
127. Zhang, J., Nguyen, Q.P., Flaaten, A.K., and Pope, G.A. 2008. Mechanisms of Enhanced

- Natural Imbibition with Novel Chemicals. Paper SPE113453 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 20–23 April. doi: 10.2118/113453-MS.
128. Determining Ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} . *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 301 (1–3): 199–208. doi:10.1016/j.colsurfa.2006.12.05
129. Zhang, H., Nikolov, A. D., & Wasan, D. 2014. EOR Using Nanoparticle Dispersions: Underlying Mechanism and Imbibition Experiments. *Energy & Fuels* **28(5)**: 3002–3009.
130. Zhang, P., Tweheyo, M.T., and Austad, T. 2007. Wettability Alteration and Improved Oil Recovery by Spontaneous Imbibition of Seawater into Chalk: Impact of the Potential Determining Ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} . *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 301 (1–3): 199–208. doi:10.1016/j.colsurfa.2006.12.058.

Chapter 4:

1. Al-Bahlani, A.M. and Babadagli, T. 2008. Heavy-Oil Recovery in Naturally Fractured Reservoirs with Varying Wettability by Steam Solvent Co-Injection. Paper SPE 117626 presented at the SPE Int. Thermal Oper. and Heavy-Oil Symp., Calgary, AB, Canada, 20-23 October.
2. Ali Karimi, A., Fakhroueian, Z., Bahramian, A. et al. 2012. Wettability Alteration in Carbonates using Zirconium Oxide Nanofluids: EOR Implications. *Energy & Fuels* **26**: 1028–1036.
3. Anderson, W.G. 1986. Wettability Literature Survey—Part I: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability. *J. Pet Tech* **38** (10): 1125–1144. SPE-13932-PA. DOI: 10.2118/13932-PA.
4. Giraldo, J., Benjumea, P., Lopera, S., et al. 2013. Wettability Alteration of Sandstone Cores by Alumina-Based Nanofluids. *Energy & Fuels* **27**: 3659–3665. DOI: 10.1021/ef4002956
5. Gupta, R. and Mohanty, K. 2011. Wettability Alteration Mechanism for Oil Recovery from Fractured Carbonate Rocks. *Transport Porous Med.* **87** (2): 635-652.
6. Elmofty, O. 2012. Surfactant Enhanced Oil Recovery by Wettability Alteration in Sandstone Reservoirs. MS thesis, Missouri University of Science and Technology.(2012).
7. Hatiboglu, C. U. and Babadagli, T. 2008. Primary and Secondary Oil Recovery from Different Wettability Rocks by Counter-Current Diffusion and Spontaneous Imbibition. *SPE Res. Eval. and Eng.* **11** (2): 418-428.
8. Hirasaki, G. and Zhang, D. L. 2003. Surface Chemistry of Oil Recovery from Fractured, Oil-Wet, Carbonate Formation. Paper SPE 80988 presented at the International Symposium on Oilfield Chemistry, Houston, TX, 5-8 February.
9. Hogshead, C.G., Manias, E., Williams, P. et al. 2010. Studies of Bitumen– Silica and Oil– Silica Interactions in Ionic Liquids. *Energy & Fuels* **25** (1): 293-299.

10. Maghzi, A., Mohammadi, S., Ghazanfari, M. H. et al. 2012a. Monitoring Wettability Alteration by Silica Nanoparticles during Water Flooding to Heavy Oils in Five-Spot Systems: A Pore-Level Investigation. *Experimental Thermal and Fluid Science* **40**: 168-176. <http://dx.doi.org/10.1016/j.expthermflusci.2012.03.004>.
11. Malham, I. B., Letellier, P., and Turmine, M. 2006. Evidence of a Phase Transition in Water-1-Butyl-3-Methylimidazolium Tetrafluoroborate and Water-1-Butyl-2, 3-Dimethylimidazolium Tetrafluoroborate Mixtures at 298 K: Determination of the Surface Thermal Coefficient, b T, P. *J. Phys. Chem. B* **110** (29): 14212-14214.
12. Painter, P., Williams, P. and Lupinsky, A. 2010. Recovery of Bitumen From Utah Tar Sands Using Ionic Liquids. *Energy & Fuels* **24** (9): 5081-5088.
13. Salehi, M., Johnson, S. J., and Liang, J. 2008. Mechanistic Study of Wettability Alteration Using Surfactants with Applications in Naturally Fractured Reservoirs. *Langmuir, The ACS Journal Of Surfaces And Colloids* **24** (24): 14099-107.
15. Standnes, D.C. and Austad, T. 2000 Wettability Alteration in Chalk 2. Mechanism for Wettability Alteration from Oil-Wet to Water-Wet using Surfactants. *J. Petr. Sci. and Eng.* **28**: 123-143.
16. Standnes, D.C. and Austad, T. 2003. Wettability Alteration in Carbonates: Low-Cost Ammonium Surfactants Based on Bio-Derivatives from the Coconut Palm as Active Chemicals to Change the Wettability from Oil-Wet to Water-Wet Conditions. *Colloids and Surfaces A* **218** (1-3): 161-173.
17. Tang, G.Q. and Morrow, N.R. 1997. Salinity Temperature, Oil Composition, and Oil Recovery by Waterflooding. *SPE Reservoir Engineering* **12** (4) 269-276.
18. Wang, Y., Xu, H., Yu, W. et al. 2011. Surfactant Induced Reservoir Wettability Alteration: Recent Theoretical and Experimental Advances in Enhanced Oil Recovery. *Petroleum Science* **8** (4): 463-476.
19. Zhang, J., Nguyen, Q.P., Flaaten, A.K. et al. 2008. Mechanisms of Enhanced Natural imbibition with Novel Chemicals. Paper SPE 113453 presented at the SPE/DOE symposium on Improved Oil Recovery, Tulsa, OK, 20-23 April.