Simulation and Experimental Wettability Studies on Low Salinity Water Injection and CO₂ Low Salinity Water-Alternating-Gas Injection

By

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Abstract

Low salinity water injection (LSWI) and CO₂ low salinity water-alternating-gas (LSWAG) injection are promising enhanced oil recovery (EOR) methods with economic and environmental advantages. Wettability alteration is considered as one of the important mechanisms. Over the past decades, there have been studies conducted to model LSWI process using shift in relative permeability curves as an indicator for wettability alteration and understand the changes in wettability induced by CO₂ and low salinity water using contact angle measurements. However, inherent limitation exits in these measurements and linking the measured contact angle to relative permeability curves for oil recovery prediction requires more research. The objective of this research is to examine whether changes in quick contact angle measurements during the injection of low salinity water or CO₂ can be used to predict oil recovery instead of conducting time-consuming core flooding or relative permeability experiments. This will be achieved first by a comprehensive literature review on CO₂ LSWAG injection to understand the mechanisms and the effect of different parameters. Secondly, the effect of temperature and interpolation techniques to relative permeability curves considering different driving forces to wettability alteration is studied. Thirdly, a newly-proposed "displacement" method for measuring contact angle is employed to study the effect of CO₂, low salinity water and injection schemes. Finally, the possibility of linking contact angle to relative permeability curves for oil recovery prediction is explored. It is found that the inclusion of hysteresis in CO₂ LSWAG injection optimization is crucial. Increasing injection temperature in the sandstone block model leads to an increase in oil recovery due to the promotion of chemical reactions with increasing temperature. The proposed "displacement" method is capable of capturing the effect of geochemical reactions and surface forces and can be used for screening optimal brine composition and injection schemes. Linking the measured contact angle to relative permeability curves has a potential for predicting oil recovery.

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Chapter 1 Introduction

As the world demand for petroleum continues to increase and the challenge of global warming rises, interest is growing in enhanced oil recovery (EOR) techniques with lower environmental impact or the use of CO₂-assisted EOR for CO₂ storage and increased oil recovery. In addition, despite the concerns for increasing oil recovery and the environment, whether the employed EOR technique is economic is also of great importance. Therefore, it is crucial to incorporate economic screening into technical investigation to determine the optimal EOR technique. The chemical EOR economic evaluation conducted by Al-Murayri et al. [1] suggests that low salinity water injection (LSWI) and CO₂ injection have economic potential by evaluating the cost per incremental barrel of oil. Low salinity water injection has been proved to be effective for improving oil recovery in both secondary and tertiary mode [2]. With the incorporation of CO₂ into LSWI and implementation as a WAG process, further incremental oil recovery could be obtained due to better mobility control [3], IFT reduction [4], and wettability alteration [5]. Thus, the two economic EOR methods targeted in this research are: (1) LSWI and (2) CO₂ LSWAG injection.

1.1 Motivation

LSWI has been under investigation for decades. Wettability alteration is considered as the main mechanism for the improved oil recovery through an interplay of several mechanisms such as increased pH and interfacial tension (IFT) reduction [6, 7], multi-component ionic exchange (MIE) [8, 9], expansion of electrical double layer (EDL) [10-12], and mineral dissolution [13]. With the addition of CO₂ into LSWI and implementation as a WAG process, further improved oil recovery is expected due to the higher CO₂ solubility in low salinity water which promotes geochemical reactions and further affects the wettability of the rock surfaces.

To investigate wettability of the rock and fluid systems, direct or indirect methods can be used. Indirect methods for characterizing rock wettability include spontaneous imbibition [14, 15], relative permeability curves [16, 17]. the Amott and Amott-Harvey index method, USBM (U.S. Bureau of Mines) method, and the combined Amott/USBM method, which measure the average wettability of the rock samples, i.e., a macroscopic mean value of the rock wettability to a given fluid. Direct method for characterizing the wettability of a specific surface is the contact angle measurement [18, 19], which gives a microscopic value of the rock wettability. On the microscopic level, according to the multi-component ion exchange (MIE) mechanism proposed by Lager et al. [20], the existence of multivalent cations in the initial formation water is essential for LSWI to be effective. However, contact angle measurements from previous studies investigating LSWI and CO₂ LSWAG injection could not capture the chemical reactions between the injected low salinity water/CO2 and formation water in one measurement. On the macroscopic level, a shift in the relative permeability curves is conserved as an indicator for wettability alteration due to LSWI [21]. The driving forces to wettability alteration could be due to decreases in salinity, MIE, or mineral dissolution. Modeling of these different driving forces and comparing their impact on oil recovery with different injection temperature needs to be further addressed. Eventually, besides linking relative permeability to salinity, equivalent fraction of Na or Ca on negatively charged exchanger (Na-X and Ca-X₂), and mineral dissolution, is there any possibility to use measured contact angles to generate relative permeability curves for oil recovery prediction with assumptions that the heterogeneity of the rock surface is not significant and residual oil saturation decreases as the wettability changes towards more water-wet?

1.2 Objectives

Based on the motivations, the objective of this study is to examine whether changes in quick contact angle measurement with the injection of low salinity water or CO_2 can be used for low salinity water or injection scheme screenings and oil recovery predictions instead of conducting time-consuming core flooding or relative permeability experiments. With these objectives, the scope of the research from the microscopic to macroscopic level is summarized in Figure 1.1.



Figure 1.1 Scope of the research

On the macroscopic level, the effect of relative permeability interpolation techniques as well as injection temperature on oil recovery, pH changes, and mineral dissolution/precipitation by LSWI are investigated. On the microscopic level, a modified contact angle measuring procedure is required to better mimic the "real" displacement process taking place in a reservoir and to better capture the geochemical reactions to study the effect of low salinity water, CO₂, and injection schemes. Moreover, comparisons among the contact angles obtained with different assumptions and conditions are needed. To link the microscopic to macroscopic level, the possibility to use the measured contact angle to generate relative permeability curves for oil recovery prediction are explored.

To achieve these objectives, I have conducted the following tasks:

- (1) A comprehensive literature review of LSWI, CO₂ WAG injection and CO₂ LSWAG injection to cover important aspects such as the working mechanism and effect of different parameters.
- (2) Modeling and comparison of different relative permeability curve interpolation techniques for LSWI at different injection temperature (20°C and 100°C), as well as their influence on oil recovery, pH, and mineral dissolution/precipitation.

- (3) Wettability studies using "displacement" method for contact measurements on the process of LSWI, and CO₂ LSWAG injection, investigating the effect of monovalent and divalent cations, CO₂, and injection schemes.
- (4) Wettability studies of LSWI using disjoining pressure considering low salinity water containing monovalent (Na⁺) or divalent (Ca²⁺) cations and exploring the possibility of linking measured contact angle to relative permeability curves to model wettability alteration.

1.3 Thesis Structure

This thesis is presented as a manuscript style and the structure is outlined as follows:

Chapter 2 presents the literature review on LSWI and CO₂ LSWAG injection. Firstly, the working mechanisms proposed for LSWI, and CO₂ WAG injection are reviewed. Subsequently, experimental studies on CO₂ LSWAG injection are presented considering different influencing factors such as CO₂ solubility in water and miscibility with oil, wettability, WAG parameters and rock compositions. Simulation work is also reviewed and an investigation on the hysteresis effect on CO₂ LSWAG injection is conducted. Research gaps are identified and summarized.

This chapter is submitted to Journal of Fuel

Chapter 3 presents a modeling investigation on three different relative permeability interpolation techniques for LSWI. These techniques include simple interpolation in terms of an aqueous component, ion exchange interpolation in terms of the equivalent fraction of an aqueous component on negatively charges surfaces, and mineral volume fraction interpolation in terms of porosity changes due to mineral dissolution/precipitation.

This chapter is ready for submission

Chapter 4 describes an experimental approach to investigate the wettability changes in terms of contact angle measurements during LSWI and CO₂ LSWAG injection. In this research we used a displacement method for measuring contact angle to evaluate wettability alteration. Our

particular interest is understanding the ion exchange and chemical reactions of the rock/oil/brine/ and rock/oil/brine/CO₂ systems by comparing the effect of monovalent and divalent ions and the effect of CO_2 on water-wet and oil-wet sandstone under different injection sequences.

This chapter is published in the conference of the Society of Core Analysis (SCA)

Chapter 5 investigated the effect of monovalent and divalent cations on wettability through intermolecular forces. Contact angles obtained from calculations based on disjoining pressure, conventional measuring method, and displacement method are investigated and compared. An alternative to relate measured contact angle to relative permeability is presented and

validated with core flooding experiments in terms of oil recovery.

This chapter is ready for submission

Chapter 6 provides the summary, conclusions, and recommendations for future work.

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Chapter 2 Literature Review of Hybrid CO₂ Low Salinity Water-Alternating-Gas Injection and Investigation on Hysteresis Effect

This chapter provides a fundamental review on LSWI, CO2 WAG injection, and CO2

LSWAG injection. It is submitted to Journal of Fuel and is under review.

Abstract

Low salinity water injection (LSWI) is considered to be more cost-effective and has less environmental impacts over conventional chemical Enhanced Oil Recovery (EOR) methods. CO₂ Water-Alternating-Gas (WAG) injection is also a leading EOR flooding process. The hybrid EOR method, CO₂ low salinity (LS) WAG injection, which incorporates low salinity water into CO₂ WAG injection, is potentially beneficial in terms of optimizing oil recovery and decreasing operational costs. Experimental and simulation studies reveal that CO₂ LSWAG injection is influenced by CO₂ solubility in brine, brine salinity and composition, rock composition, WAG parameters, and wettability. However, the mechanism for increased recovery using this hybrid method is still debatable and the conditions under which CO₂ LSWAG injection is effective are still uncertain. Hence, a comprehensive review of the existing literature investigating LSWI and CO₂ WAG injection, and laboratory and simulation studies of CO₂ LSWAG injection is essential to understand current research progress, highlight knowledge gaps and identify future research directions. With the identified research gap, a core-scale simulation study on hysteresis effect in CO₂ LSWAG injection is carried out. The results indicate different changing trend in oil recovery due to the impact of salinity on hysteresis and excluding of hysteresis effect in CO2 LSWAG injection simulation and optimization might lead to significant errors.

Keywords: Low salinity water injection (LSWI); CO₂ WAG injection; CO₂ LSWAG injection; hysteresis effect.

2.1 Introduction

Maximizing oil recovery from existing reservoirs plays a significant role in increasing profitability and sustainability of the oil and gas industry. However, around 70% of the global oil reserves cannot be recovered by conventional oil recovery techniques [1]. Therefore, various oil recovery methods to achieve higher production have been implemented worldwide. Enhanced oil recovery (EOR) methods such as chemical flooding (using polymers, alkaline and/or surfactants), miscible flooding (CO₂, nitrogen and liquefied petroleum gases), thermal flooding (using steam), microbial flooding (microorganisms) or water-alternating-gas (WAG) injection may increase oil recovery by 5-20% of OOIP [2] depending on the specific reservoir conditions. Technical practicability of an EOR method must be coupled with an evaluation of its economic feasibility, especially during a time when the oil price is low. The chemical EOR economic evaluation conducted by Al-Murayri et al. [3] suggests that low salinity water injection (LSWI) and CO₂ injection have economic potential and both of these methods have been confirmed to be effective for increasing oil recovery in both secondary and tertiary mode [4, 5]. In order to achieve even higher oil recovery at low cost, a new hybrid technique was developed in the last 15 years to incorporate low salinity water (LSW) into CO₂ WAG injection under both miscible and immiscible conditions [6-9]. This EOR method, termed CO₂ low salinity (LS) water-alternating-gas (WAG) injection in this paper, combines the effect of LSWI with CO₂ injection to enhance both macroscopic and microscopic sweep efficiency. The experimental and simulation studies [7, 8, 10] showed that the ultimate oil recovery using CO₂ LSWAG injection was higher than using LSWI and CO₂ WAG injection alone. Despite the EOR potential of CO₂ LSWAG injection, some results are contradictory [11, 12], where reduced oil recovery factor were reported for CO₂ LSWAG injection. To the best of our knowledge, no systematic reviews were found on CO₂ LSWAG injection that cover the influence of CO₂ solubility in brine, salinity and composition of brine, rock composition, WAG parameters, and wettability. Therefore, a thorough review on the EOR potential of CO_2 LSWAG injection will contribute to the understanding of this hybrid EOR technique and provide insights into future studies.

This literature review covers research studies related to LSWI, CO_2 WAG injection and CO_2 LSWAG injection. The fundamentals of CO_2 WAG injection and LSWI in sandstone and carbonate are presented, including basic theory and mechanisms. Laboratory studies of CO_2 LSWAG injection, including the effect of different parameters are reviewed, followed by simulation work, considering complex geochemical reactions, geological uncertainties, and optimization. Based on the laboratory studies, the proposed mechanisms and working condition of CO_2 LSWAG injection are addressed along with identified research gaps. In the end, to fill the void of the hysteresis study on CO_2 LSWAG injection, we have conducted core-scale simulation investigations on the impact of hysteresis under different salinities with two-phase Carlson model and three-phase Larsen and Skauge model.

2.2 CO₂ WAG Injection

A WAG process entails the injection of alternating cycles of gas slug and water slug at certain slug size and WAG ratio into the reservoir. As the gas is injected into the reservoir and contacts the oil, a reduction in oil viscosity as it contacts the oil is expected, which makes the oil more mobile and easier to flow. The mobility ratio (M) is generally defined as the mobility of the displacing fluid (λ_{ing} , water/gas) divided by the mobility of the displaced fluid (λ_{ed} , oil) [13]:

$$M = \frac{\lambda_{ing}}{\lambda_{ed}}$$
(1)

If the mobility ratio is less than or equal to 1 ($M \le 1$), the displacement front tends to be stable, otherwise (M > 1), the further M is from 1, the less stable and favorable is the displacement. In a continuous gas injection, the mobility ratio of injected gas and oil bank, which is the gas mobility divided by oil mobility, is generally very unfavorable. Thus, a technique to overcome this problem was developed, in which slugs of water and gas are injected alternately. The injection of water decreases the mobility ratio compared to the injection of gas alone; hence, mobility ratio in the process is improved. Gravity segregation induced by the density differences between the gas and fluid phase is another important mechanism. Due to gravity forces, waterflooding is more likely to sweep the lower part of a reservoir and injection of gas sweeps more of the upper parts. Holm and Josendal [14] and Perera et al. [15] listed the characteristics which enables CO_2 to remove oil from the reservoir effectively (Figure 2.1), including the effect of CO_2 characteristics on oil phase, brine phase and reservoir rock. CO_2 promotes oil swelling and viscosity decrease. The formation of carbonic acid (H₂CO₃) could lead to dissolution of carbonate, which further increases porosity and permeability near the injection zone [16]. This acidic effect also contributes to the stabilization of negatively charged clay particles [17].



Figure 2.1 Effect of CO₂ characteristics on oil/brine/rock

Generally, during a CO_2 WAG injection process, utilization of CO_2 can achieve enhanced oil recovery through either miscible or immiscible process. The development of miscibility between injected CO_2 and reservoir oil is dependent on several factors, such as the pressure and temperature of the reservoir, and properties of reservoir oil, including API gravity, molecular weight, and composition of oil (i.e., concentration of intermediate components, or C_{7+} fraction) [18].

2.2.1 Miscible Process

In the oil recovery process of gas injection, the injected gas will develop first contact or multiple contact miscibility with the oil [15]. First contact refers to the process that the injection of the solvent forms a single phase upon first contact that is miscible with the crude oil and, typical for recovering light oil using liquified petroleum gases (LPG). The latter process achieves miscibility with different contacts as the fluids move through the reservoir by vaporizing and condensing gas drive, typical for solvents like CO_2 [19].

Among the factors that affect CO_2 miscibility in oil, pressure of the reservoir is the most important and a key parameter for determining miscibility [20, 21]. Generally, miscibility between CO_2 and reservoir oil is achieved with pressure above the minimum miscible pressure (MMP). The CO_2 miscible process is illustrated in Figure 2.2, showing a transition zone, miscible with the forefront reservoir oil and the injected pure CO_2 near injection well. Jarrell et al. [22] demonstrate a development of transition zone with no interface by the mass transfer between reservoir oil and CO_2 . Two processes are considered as the miscibility development of CO_2 with reservoir oil: (1) condensing gas drive; and (2) vaporizing gas drive. In the former process, the injected CO_2 dissolves into the reservoir oil, forming dynamic miscibility. In the latter process, reservoir oil component with intermediate-to-high molecular weight vaporizes into CO_2 , and form miscibility under certain conditions.



Figure 2.2 Schematic CO₂ miscible process (adapted from Verma [19])

2.2.2 Immiscible Process

 CO_2 is unlikely to develop miscibility if the reservoir pressure is below the MMP or the composition of reservoir oil is unfavorable (i.e., heavy oil) [19]. Under these circumstances, CO_2 and oil will not form a single phase. With immiscible CO_2 WAG injection, improved oil recovery is achieved by oil swelling and viscosity reduction induced by dissolution of CO_2 into reservoir oil. Thus, CO_2 solubility in the reservoir oil is a key factor for effective implementation of immiscible CO_2 WAG injection. CO_2 solubility in oil can be affected by saturation pressure, temperature of the reservoir, and composition of oil [23, 24]. As pressure increases or temperature decreases, CO_2 solubility in oil increases. However, as the temperature is lower than CO_2 critical temperature, CO_2 solubility is also affected by oil composition and liquefaction, where gaseous CO_2 is more soluble in crude oil than liquid CO_2 [25-27]. Commonly recognized oil recovery mechanisms for the immiscible CO_2 displacement process include oil swelling and viscosity reduction [28-31], IFT reduction [32, 33], and blowdown [14, 32, 34].

2.2.3 Hysteresis

During CO₂ WAG injection process, changes in saturation of water and CO₂ are expected after each injection cycle in a multiphase flow. Due to the alternating injection cycles of water and gas, saturation of water and gas will increase and decrease alternately, which generates a hysteresis loop. This hysteresis phenomena can be seen in both capillary pressure and relative permeability, represented by drainage and imbibition processes. The cyclic WAG process could induce favorable hysteresis relative permeability effect which assists in reducing the mobility of gas to achieve superior conformance control and higher ultimate sweep efficiency [35]. Generally, the three-phase hysteresis effect is more pronounced in immiscible WAG process than miscible WAG process [36] and its impact is more significant with non-wetting phase (gas) than wetting or intermediate wetting phase [37].

2.3 Low Salinity Water Injection (LSWI)

Low salinity effect (LSE) was first discovered by Bernard [38] in 1967 when he observed that oil recovery in formations containing hydratable clays increased as the concentration of the injected sodium chloride brine was decreased from 1% to 0.1%. Subsequently, researchers and companies worldwide have studied LSE and confirmed that injection brine composition and salinity can have an enormous impact on oil recovery [39-55].

2.3.1 Proposed Mechanism of LSWI in Sandstone

Even though numerous works has been conducted to investigate the underlying mechanism of LSWI, there is no consistent explanation and LSE might be a result of several proposed mechanisms acting together. One reason is because of the complex compositions or structures of the aqueous phase, oil phase and rock minerals. Another reason is the complex geochemical interactions between/among all these phases [56]. Figure 2.3 summarizes some of the proposed LSWI mechanisms and their related effects in sandstone. These mechanisms were postulated

from either direct pore-scale and nano-scale observations or indirect measurements such as pH and ion concentration measurements from core scale and field scale.



Figure 2.3 Overview of some proposed mechanisms of LSWI in sandstones Fines migration can be induced by the poorly-cemented clay minerals [57] or release of mixwet particles [42]. These released fines will migrate with fluid flow to zones with higher permeability and lodge in smaller pores or pore throats, resulting in diversion of the flow path to unswept zones with lower permeability. Hence, sweep efficiency is improved [42, 58]. Insitu increase in alkalinity [59] arising from the differences in cation affinity to negatively charged surface [60] gives rise to IFT reduction, surfactant-like behavior and chemical reactions for oil detachment [59, 61]. Osmotic effect is generated by the difference in chemical potential of a system containing low and high salinity solutions with a semipermeable membrane in between. This difference acts as a driving force for the movement of water and oil relocation [62-66]. Additional oil recovery by LSWI is often observed with wettability alteration towards more water-wet [51, 67-70]. The proposed mechanisms related wettability alteration are multi-component ionic exchange (MIE) [71, 72], expansion of electrical double layer [48, 73, 74], salt-in effect [54], and mineral dissolution [75]. For a detailed review and discussion on the mechanisms, readers can refer to the work conducted by Sheng [4], Rezaeidoust et al. [54], Katende and Sagala [76], Al-Shalabi and Sepehrnoori [77], and Yue et al. [78].

2.3.2 Proposed Mechanism of LSWI in Carbonate

In carbonate reservoirs worldwide, less than 30% of oil has been recovered due to low permeability, natural fractures, inhomogeneous rock properties and more than 80% of the carbonate reservoirs are intermediate or oil-wet [79, 80]. Compared to the complexities of LSE in sandstone, the most acceptable working mechanism of LSWI in carbonate is the wettability alteration from oil-wet to intermediate or water-wet due to changes in rock surface charge and microscopic dissolution of anhydrite (Figure 2.4) [77, 81-83].



Figure 2.4 Summary of proposed mechanisms of low salinity water injection in carbonates *Changes in rock surface charge.* Ca^{2+} , Mg^{2+} and SO_4^{2-} are the determining ions for wettability alteration in carbonate reservoir. For seawater injection in chalk, the adsorption of SO_4^{2-} to the chalk surface lowers the positive charge on rock surface and electrical repulsion; thus, more Ca^{2+} will be attached to the chalk surface and react with the carboxylic group, promoting the detachment of the organic carboxylic materials [84-86]. At higher temperature, the reactions between the ions and rock surface become more pronounced, making Mg^{2+} capable of substituting Ca^{2+} on the rock surface, [87, 88], leading to more detachment of oil. Subsequently, Yousef et al. confirmed LSE in carbonate as a result of wettability alteration and the effect of

IFT reduction is negligible [89, 90]. Low salinity water with a significant reduction in the concentrations of Na⁺ and Cl⁻ is the key to trigger wettability alteration in carbonate reservoirs [55, 83, 89].

Mineral dissolution. Mineral dissolution during flooding could result in secondary pore structure and potentially expelling of oil [77]. Additionally, the microscopic dissolution of anhydrite occurring during injection of low salinity water leads to in-situ generation of SO_4^{2-} which promotes wettability alteration [83, 91].

2.4 CO₂ LSWAG Injection

Based on the review on LSWI and CO_2 WAG injection, it is possible to combine the strength of these two methods to alter wettability and enhance CO_2 mobility; thus increasing oil displacement efficiency. A comprehensive review of CO_2 LSWAG laboratory and simulation studies has been completed; it is presented accordingly with proposed mechanisms.

2.4.1 Laboratory Observations of CO₂ LSWAG Injection

Over the past 15 years, core flooding experiments have been carried out to investigate CO₂ LSWAG injection in both sandstone and carbonate. The EOR potential of CO₂ LSWAG injection is shown in light-to-heavy crude oil. Most results confirmed improved oil recovery using this hybrid technique, in both secondary and tertiary modes, with some exceptions [11, 12]. Studies with negative or neutral outcomes used core samples that were either not aged or aged for just three days, which would lead to a strongly water-wet initial wettability. This initial condition is not favorable for low salinity water to be effective [67, 68]. Moreover, the salinity of injection adopted in the core flooding experiments by Jiang et al. [12] is 10000 ppm, which lies beyond the range suggested for LSWI (1000 - 5000 ppm) [59]. It can be seen that the success of a CO₂ LSWAG process is dependent on a variety of parameters, hence, the effects of injection brine composition and salinity, rock composition, miscibility, WAG parameters,

solubility of CO_2 in brine, and wettability alteration on oil recovery enhancement are reviewed and discussed in this section.

2.4.1.1 Effect of Miscibility

Based on a WAG injection field review by Christensen et al. [92], higher oil recovery is generally achieved by miscible or near-miscible WAG injection in comparison with the immiscible process. However, the investigation of the importance of miscibility on gas flooding conducted by Thomas et al. [93] suggests that miscibility might not be necessary for increasing oil recovery as long as the IFT has been reduced to a desired level, which is identified as the level to effectively enhancing oil recovery. It is noteworthy that this conclusion is dependent on the interplay between mobility and IFT, which determines the success of a WAG process [5, 93].

Up to date, only one study was found on the investigation of miscibility effect during $CO_2 LS$ and HS WAG injection. Kulkarni et al. [94] conducted core flooding experiments on Berea sandstone. The oil phase used is n-decane and the aqueous phase are two brines (5% NaCl and Yates reservoir brine). Pure CO_2 is used as the injection gas under miscible and immiscible conditions. Their results, shown in Table 2.1, indicate that miscible CO_2 WAG injection yields higher oil recovery than the immiscible process. However, it is worth noting that the oil phase used in this study is n-decane, which is non-polar. Therefore, the difference between miscible and immiscible displacement could be mainly ascribed to the effect of CO_2 miscibility with oil, and LSW might not play a role for improving oil recovery [95].

able	e 2.1 Oil recovery comparison between miscible	e and immiscible wAC	j injectio
	Experiment title	Recovery %OOIP	
	WAG - immiscible (NaCl brine)	8.3%	
	WAG - miscible (NaCl brine)	36.6%	
	WAG – immiscible (Yates reservoir brine)	9.9%	
	WAG – miscible (Yates reservoir brine)	25.4%	

Table 2.1 Oil recovery comparison between miscible and immiscible WAG injection [94]

2.4.1.2 Effect of CO₂ Solubility in Brine

Previous experimental and modeling studies demonstrate that CO₂ solubility in brine increases with decreases in salinity [10, 96-98]. This increment of CO₂ solubility with low salinity water can result in improved oil recovery through CO₂-brine IFT reduction [10]. Bennion and Bach [99] conducted regression analysis on the correlation of IFT of CO₂ and brine with reservoir pressure, temperature, and CO₂ solubility. Their results showed that the IFT of CO₂ and brine decreases with increasing CO₂ solubility in brine. Yang et al. [100] used the axisymmetric drop shape analysis technique to obtain the IFT of the crude oil, reservoir brine, and CO₂ systems at 27 and 58°C and pressures up to 31 MPa. They found that IFT_{brine-oil} reduced as CO₂ was introduced to the system. Moreover, the reduction in $IFT_{CO_2-brine}$ and $IFT_{oil-brine}$ was observed with increasing pressure or increasing CO₂ solubility. Thus, with the injection of LSW and CO₂, solubility of CO₂ in LSW is higher, which might promote enhancement of oil recovery by reduction in IFT. From the study performed by Zolfaghari et al. [8], a 5% increase in oil recovery was observed using CO₂ LSWAG injection compared to LSWI alone at the same pore volume of injection, indicating the low pH buffer solution developed by the dissolution of CO₂ in LSW has positive impact on oil recovery. The reduction in $IFT_{CO_2-brine}$ with increasing CO₂ solubility may contribute to the enhancement of oil recovery in this case. Chaturvedi et al. [9] investigated the impact of salinity (1-4 wt% NaCl brine) on CO₂ absorption under 4, 8 and 12 bar confining pressures at 50 and 80°C. The dominant absorption of polar gas CO₂ is physisorption, where CO₂ is trapped in the form of bubbles and encapsulated by layers of water [9]. A small part of the gas molecules reacts with water, and the following reactions will take place to produce carbonic acid (H_2CO_3) and HCO_3^- and CO_3^{2-} ion.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \tag{5}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{6}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \tag{7}$$

The CO_2 molality, moles of CO_2 absorbed in a solvent, as a function of salinity is depicted in Figure 2.5, showing that CO_2 absorption decreases with increasing salinity and temperature, and decreasing pressure.



Figure 2.5 CO₂ molality results for different salinities (0-4 wt% NaCl); (a) 50°C; (b) 80°C [9] They used the Young-Laplace equation of capillarity to calculate the IFT between CO₂ and brine [101]. As shown in Figure 2.6, the interfacial tension of brine and CO₂ decreases with decreasing salinity and increasing temperature and pressure. Chaturvedi et al. [9] claimed that the decrease in IFT is ascribed to the increasing CO₂ solubility in water with increasing pressure and decreasing salinity at the same temperature and pressure, with one exception of the IFT measured at 80 °C, 12 bar and with 2 wt% NaCl. The conducted CO₂ LS WAG core flooding experiments recommended the use of low salinity water (1 and 2 wt% NaCl) in conjunction with CO₂ injection to improve oil recovery [9].



Figure 2.6 CO₂- brine solution interfacial tension at different pressure (4-12 bar) and temperature of (a) 50°C; (b) 80°C [9]

2.4.1.3 Effect of Brine Composition and Salinity

The salinity of injection brine is an influential parameter in the oil recovery process, as confirmed by several numerical and experimental investigations [41, 43, 102, 103]. Jiang et al. [12] conducted CO₂ LS and HS WAG core flooding experiments with model oil (n-decane and n-hexadecane) and reservoir oil. The Berea sandstone core samples were aged for three days at reservoir temperature (60° C). Alternating cycles of CO₂ and brine with slug size of 0.5 PV and a WAG ratio of 1:1 were applied in every core flooding test. In the CO₂ HS WAG flooding experiments with model oil, 1000 ppm NaCl was used as formation brine. The salinities of injection NaCl brine were 1000, 2000, 4000, 8000, 16000, and 32000 mg/L. The effect of divalent cations was investigated by comparing the oil recovery factor with injection brine with 8000 ppm NaCl and 4000 ppm NaCl + 4000 ppm CaCl₂. Their results show that the recovery factor of the tertiary mode increases slightly with elevated injection brine salinity, with no signs of ionic exchange. It is suggested that the decrease of CO₂ solubility in high salinity brine is responsible for the higher oil recovery. They also found that the effect of divalent cations Ca²⁺ in the injection brine is similar to that of Na⁺ based on the comparison between the oil
recoveries with injection of 8000 ppm NaCl or 4000 ppm NaCl + 4000 ppm CaCl₂. However, it is worth pointing out one of the drawbacks of the experimental design that the oil used is non-polar, therefore, the ligand bonding or cation exchange suggested by Lager et al. [71] for LSE to occur might not be able to take place. Therefore, the conclusion that effect of Ca²⁺ and Na⁺ is similar is not generalized. In their LS and HS WAG injection experiments with crude oil, 20,000 ppm NaCl + 10,000 ppm CaCl₂ is used as formation brine. The salinities for injection brines are 10,000, 16,000 and 32,000 ppm, a combination of 66.67% NaCl and 33.33% CaCl₂. The recovery factors of WAG injection as tertiary mode increase slight with salinity, from 38% to 40%, however, the overall recovery factor decreases with salinity. From their experiments, the effectiveness of CO₂ LSWAG injection is certainly dependent on several factors, such as composition of oil and brine. However, we cannot simply draw a conclusion that CO₂ HSWAG injection is more effective in terms of EOR since the LSW used in the water cycle is not within the salinity range recommended [59].

On the other hand, Zolfaghari et al. [8] obtained different results with similar core flooding experiments on kaolinite-free core samples. The samples were aged for two days in heavy oil (with 6.5% asphaltene content) at 70°C before flooding. Synthetic brine concentrations of 1000 ppm (20% CaCl₂+80% NaCl) and 50000 ppm (20% CaCl₂+80% NaCl) were used. Five WAG cycles with 0.16 PV slug size and WAG ratio of 1:1 were applied for each CO₂ LSWAG injection (secondary mode). The LSE was observed in all experiments despite the fact that the core samples are free of kaolinite and only aged for two days. The authors ascribed the observed EOR effect to CO₂ and its buffer effect in the presence of water. They argue that this buffer effect induced by CO₂ casts doubt on the mechanism proposed by McGuire et al. [61], that LSWI is like alkaline flooding. This positive influence of low salinity water in heavy oil indicates that the application of CO₂ LSWAG injection may not be limited to light-to-medium oil reservoirs. AlQuraish et al. [104] investigated CO₂ low salinity (LS) and high salinity (HS) WAG injection as tertiary recovery to explore the effect of salinity and brine composition. In their study, synthetic formation water at 20 wt% salinity, seawater (acting as high salinity water, HSW), and 10-time diluted seawater (acting as low salinity water, LSW) were used as the aqueous phase. Detailed information of the brine compositions can be found in Table 2.2. The oil phase was light crude oil. They conducted LSW and HSW flooding as secondary recovery, followed by miscible CO₂ LS and HS WAG injection. The results show that incorporating LSW into miscible CO₂ WAG injection is effective in providing 18.7% higher incremental oil recovery compared with the use of HSW in Berea sandstone.

	1 6		
Parameter	FB Formation brine	HSW Seawater	LSW
Calcium, mg/L	28035.05	522	51
Magnesium, mg/L	5241.18	1624	140
Sodium, mg/L	51809.52	13416	1220
Potassium, mg/L	-	507	45
Chloride, mg/L	112365.25	23321	2057
Total Alkalinity (as CaCO ₃)	-	7993	707
Sulfate, mg/L	-	3479	378
Nitrate, mg/L	-	<1	<1
Fluoride, mg/L	-	1.8	0.17
Total Dissolved Solids (TDS), mg/L	197,451	36,170	3,360
pH	7.37	6.90	7.05
Density @ 60°C & 14.7 psi	1.038	1.021	0.993
Viscosity @ 60°C & 14.7 psi	1.031	0.863	0.657

Table 2.2 Composition of brine [104]

Legends: (1) FB – formation brine; (2) HSW – high salinity water; (3) LSW – low salinity water

The depletion of monovalent ions and dilution of multivalent ions during injection of modified seawater (detailed composition can be found in Table 2.3) was studied by Al-Saedi et al. [105]. Their results (Table 2.4) showed that injection brine without NaCl resulted in 10% more oil recovery than seawater flooding. They also found that diluting the Ca²⁺ concentration fives and depleting NaCl in the injection brine could increase 19.25% oil recovery and if it is injected alternatively with CO₂, further enhancement in oil recovery could be expected. It is suggested that dilution of Ca²⁺ ions assist in improving oil recovery by shifting the following reaction

towards the right direction [106], resulting in more desorption of oil from the negatively charged surfaces.

$$Clay - Ca^{2+} + H_2 0 \rightleftharpoons Clay - H^+ + Ca^{2+} + 0H^-$$
(9)

Even though these modifications are conducted on seawater, these results suggest that it might be possible to achieve higher oil recovery in CO_2 LSWAG injection with the manipulation of ion compositions and WAG process is more efficient compared to modified seawater and continuous CO_2 injection. It can be inferred that further dilution of Ca^{2+} or depleting Ca^{2+} in LSW might improve oil recovery even more when injected alternatively with CO_2 .

		-		5		<u> </u>
Compound	FB	SW	SW	MSW1	MSW2	MSW3
			-0NaCl	0NaCl-d _{5Ca}	0NaCl-d _{5Mg}	0NaCl-d5 _{SO4}
NaCl	81,000	25,000	0	0	0	0
CaCl ₂	17,000	2,000	2,000	400	2,000	2,000
MgCl ₂	5,000	10,500	10,500	10,500	2,100	10,500
Na ₂ SO ₄	-	4,900	4,900	4,900	4,900	980
KCl	1,000	-	-	-	-	-
TDS	104,000	43,400	18,400	15,800	9,000	13,480

Table 2.3 Composition of the formation and injected brine [105] (mg/L)

Legends: (1) 0NaCl – without NaCl; (2) $0NaCl-d_{5Ca}$ – without NaCl and 5-time diluted Ca^{2+} ; (3) $0NaCl-d_{5Mg}$ – without NaCl and 5-time diluted Mg^{2+} ; (4) $0NaCl-d_{5SO4}$ – without NaCl and 5-time diluted SO_4^{2-} ; (5) FB – formation brine; (6) SW – seawater; (7) MSW –modified seawater

Flooding Sequence	Recovery %OOIP
2 PV SW	43.64
2 PV SW, 5 PV CO ₂	47.64
2 PV SW, 3 PV SW-0NaCl, and 5 PVCO ₂	52.70
2 PV SW, 3 PV MSW1, and 5 PV CO ₂	63.45
2 PV SW, 3 PV MSW2, and 5 PV CO ₂	58.65
2 PV SW, 3 PV MSW3, and 5 PV CO ₂	55.83
2 PV SW, 3 PV MSW1/CO ₂ (3 cycles, 0.5 PV slug size)	68.14

Table 2.4 Recovery factor of different flooding sequences [105]

Al-Abri et al. [107] studied the performance of immiscible CO₂ LSWAG injection in sandstone cores with different brine compositions; 5000 ppm NaCl, 5000 ppm KCl and 5000 ppm MgCl₂ as three different injection brines. Their results show that injection of NaCl brine yields the highest oil recovery, followed by MgCl₂ and KCl brine. CO₂ solubility is found to be lowest in 5,000 ppm NaCl and highest in 5,000 ppm KCl. Even though the authors suggest that MIE

mechanism of Na⁺ replacing the divalent cations, less CO₂ solubility in NaCl LSW could also be one cause.

2.4.1.4 Effect of Rock Composition

AlQuraish et al. [104] performed miscible CO₂ LSWAG injection in Berea and Bentheimer sandstones to investigate the effect of rock composition. Both samples were primarily composed of quartz with kaolinite clay, 2% kaolinite for Berea and 0.5% kaolinite for Bentheimer. CO₂ LSWAG injection outperformed CO₂ HS (high salinity) WAG injection in the Berea core samples in terms of oil recovery, whereas CO₂ HS WAG injection results in higher oil recovery in the Bentheimer core samples (Table 2.5). This observation indicates that the presence of clay minerals, especially kaolinite, might be essential for CO₂ LSWAG injection to be effective. The experiments of LSWI conducted at core scale [42] and pore scale [58] suggested that the migration of fine particles (especially kaolinite) might be a contributor to improved oil recovery in sandstones.

Table 2.3 Comparison of total recovery for Berea and Benthemer core samples [104]				
Rock Type Description of Experiment Total Recovery %				
Berea Sandstone	CO ₂ HS WAG Injection	65.20		
	CO ₂ LS WAG Injection	82.40		
Bentheimer Sandstone	CO ₂ HS WAG Injection	85.18		
	CO ₂ LS WAG Injection	72.65		

Table 2.5 Comparison of total recovery for Berea and Bentheimer core samples [104]

Zolfaghari et al. [8] cast doubt on considering kaolinite migration as a key mechanism in LSWI since the core samples they used in their experiments are free of kaolinite, and additional oil recovery is observed. In a pore-scale visualization of LSWI performed by Amirian et al. [108], fines migration was reported to play an insignificant role. Further investigations are required to better understand the roles of clays in CO₂ LSWAG injection.

2.4.1.5 Effect of WAG Parameters

Generally, WAG parameters include WAG ratio, slug size and WAG cycle. It is necessary to regulate the slug size of injected water and gas and determine the optimum WAG ratio and cycle to achieve the best displacement efficiency. Selecting of unfavorable parameters in a WAG process would possibly lead to low oil recovery. Therefore, it is essential to conduct optimization and sensitivity studies before initiating a WAG process.

Le Van et al. [109] investigated the effect of slug size (0.2, 0.4, 0.6 PV) and salinity (1000, 2000, 3000, 4000 and 5000 ppm NaCl) on CO₂ LSWAG injection using core flooding experiments and response surface methodology (RSM) to optimize the variables. Their results indicate that the optimal oil recovery by RSM was achieved with 0.455 PV of slug size and 4313 ppm NaCl injection brine. However, this optimization of CO₂ LSWAG injection is a simple approach and cannot be generalized. Dang et al. [7] conducted robust optimization on CO₂ LSWAG injection under geological uncertainties [110] considering WAG parameters, brine composition, injection pattern location and bottom hole pressure (BHP) of production wells. Net present value (NPV) is the objective function and realizations are generated with varying distribution of facies and clay content. DECE (Designed Exploration Controlled Evolution) optimization method [111, 112] is employed for finding the optimal results. WAG ratio is found to have significant effect on ultimate oil recovery and the highest is achieved with WAG ratio of 1:2. They claim that due to the higher CO₂ solubility in LSW, make-up of CO₂ is needed to achieve higher oil recovery. Therefore, WAG ratio of 1:2 is found to be optimum in their study. Zekri et al. [113] conducted miscible CO₂ HS and LS WAG injection in carbonate cores using different WAG ratios (1:1, 2:1, and 1:2). The comparison among these cases in terms of oil recovery is shown in Figure 2.7. WAG ratio 1:2 yields highest oil recovery and WAG ratio of 2:1 results in lowest irrespective of salinity difference. LSE is hindered while employing WAG ratio of 1:1 and the best synergy of LSW and CO2 is achieved with WAG ratio of 1:2. Therefore, a WAG ratio of 1:2 is considered as the optimum in their case. This finding is in accordance with the optimization conducted by Dang et al. [7].



Figure 2.7 Effect of WAG ratios on oil recovery in CO₂ HS and LS WAG injection [113] Since limited studies on CO₂ LSWAG optimization or effect of WAG parameters are found from literature so far, thus, it would be beneficial to refer to other WAG injection optimization work for identifying potential research topic. Chen et al. [114] performed miscible CO₂ WAG optimization using stochastic algorism GA (genetic algorithm) to locate optimum solution of WAG ratio and cycle, injection rates and BHP of producer. Their results suggest an optimum WAG ratio of 1:2 and the sensitivity study show that finding an optimal gas slug size assists in maximizing oil recovery. Mohagheghian et al. [115] used GA and PSO (particle swarm optimization) for optimization and sensitivity studies, showing that WAG ratio of 0.15 for maximized oil recovery and 0.9 for maximized NPV. To overcome the time-consuming drawback of conventional optimization methods which are as function of time, light mathematical Proxy models are developed for WAG parameter optimization, which outputs NPV or oil recovery at a given time [116]. They found that a WAG ratio of 2.85 results in highest oil recovery in their case. These results differ from the optimum ratio of 1:1 reported from laboratory experiments [117-119] and most field applications [5, 92] for WAG injection (without incorporating LSW). This could be caused by neglecting affecting factors such as reservoir heterogeneity or gravity forces. Additionally, with the incorporation of LSW into CO₂ WAG injection, the difference of CO₂ solubility in HSW and LSW would potentially lead to employing WAG ratio lower than 1, indicating that larger injection volume of gas could contribute to EOR of CO₂ LSWAG injection. However, whether lowering WAG ratio to less than 1 is optimum in increasing oil recovery requires more laboratory experiments on CO₂ LSWAG injection.

2.4.1.6 Effect of Wettability

According to Anderson [120], wettability is the main factor which governs the fluids distribution, the flow path and the location. Generally, the wetting state of a rock surface is affected by salinity, mineralogy of the rock, crude oil content, temperature and pressure, pH of formation and injected brine, and gas in solution. Teklu et al. [10] performed contact angle measurements between reservoir sandstone core discs to mimic a condition of miscible CO₂ flooding with seawater and low salinity water (Figure 2.8). The measurement condition A, B, and C are described in Table 2.6.



Figure 2.8 Contact angle between sandstone and oil-droplet at conditions A, B, and C [10]

	Table 2.0 Measurement condition A, B and C [10]
Condition A	 Core disc was aged for three weeks at reservoir temperature Seawater is between the disc and oil-droplet during contact angle measurement
Condition B	 Aged disc was kept in a piston with seawater and CO₂ for 2 days Seawater and CO₂ is between the disc and oil-droplet during contact angle measurement
Condition C	 Aged disc was kept in a piston with low salinity water and CO₂ Low salinity water and CO₂ is between the disc and oil-droplet during contact angle measurement

Table 2.6 Measurement condition A, B and C [10]

As brine salinity decreases, the solubility of CO_2 increases, forming in-situ carbonated water of higher CO_2 saturation in the brine phase. This leads to IFT reduction and wettability alteration of rock towards hydrophilic; hence, improved oil recovery [10]. Similar results were observed from Almeida da Costa et al. [121]. They performed contact angle and IFT measurements in the crude-oil/CO₂/water/rock system at 725 psi and 2610 psi, and 60°C. As shown in Figure 2.9, the IFT between crude oil and CO₂ decreases with increasing pressure, indicating enhanced molecular interactions, and also contributes to increased oil mobility [121]. The observation of a reduction in water contact angle as pressure increases indicates that the rock surface becomes more water-wet while CO₂ migrates towards the oil-water interfaces, resulting in the swelling of the oil drop over time.



Figure 2.9 (a) IFT of crude oil/CO₂; (b) Contact angle as a function of time and pressure in a low salinity brine/CO₂ system at 60°C (adapted from Almeida da Costa et al. [121])

Al-Abri et al. [107] investigated the wettability alteration by CO₂ LSWAG injection based on the calculated wettability index (WI) from contact angle measurements. The definition of WI is defined as

$$WI = \frac{\theta_{original} - \theta_{final}}{\theta_{original} - \theta_{initial}}$$
(10)

where, $\theta_{initial}$ is the contact angle obtained after samples have been aged in base brine, $\theta_{original}$ is the contact angle obtained after samples have been aged in crude oil, and θ_{final} is the contact angle obtained after samples have been aged in brine with different salinities. Their results are shown in Table 2.7. A WI greater than one means more water-wet compared to the initial condition. The experimental results demonstrate that a favorable wettability alteration is achieved by NaCl and KCl brine compared to MgCl₂ brine (see Table 2.7, samples 3, 5 and 7). Moreover, as CO_2 is incorporated into low salinity water, the wettability index increased and the final contact angle decreased (Table 2.7), indicating the alteration of wettability towards more water-wet. They also conducted three tertiary CO_2 LSWAG core flooding experiments with high salinity flooding as secondary recovery. The lowest oil recovery (43.5%) was obtained in the combined injection of CO_2 and KCl brine, which has the lowest wettability index. This suggests that the wettability alteration by the interactions between LSW, CO_2 and rock minerals could be one of the contributors to improved oil recovery.

 $\boldsymbol{\theta}_{initial}$ WI Sample No. **Brine** $\theta_{original}$ $\boldsymbol{\theta}_{final}$ 51.24 HS (50,000 ppm) 118.19 71.43 0.70 1 2 HS (50,000 ppm) - CO₂ 51.24 114.33 42.12 1.14 3 NaCl (5,000 ppm) 51.24 133.85 36.44 1.18 NaCl (5,000 ppm) - CO2 4 118.78 33.34 51.24 1.27 5 KCl (5,000 ppm) 51.24 109.45 41.95 1.16 6 KCl (5,000 ppm) - CO₂ 51.24 122.33 43.58 1.11 7 MgCl₂ (5,000 ppm) 51.24 52.37 0.98 126.21 8 MgCl₂ (5,000 ppm) - CO₂ 51.24 101.23 35.26 1.32 Legends: HS – High Salinity Brine

Table 2.7 Value of contact angle and wettability index [107, 121]



Figure 2.10 Contact angle measurements for sandstone after being saturated with oil, brine and CO₂ at 45°C [122]

Data from wettability studies of CO₂-enriched brine, sandstone and crude oil is very limited. In all cases, CO₂ and brine typically exist as a single phase, forming in-situ carbonated water. The study of salinity effect on contact angle in the CO_2 /brine/oil system by Ameri et al. [122] showed that wettability of the substrate was altered from strongly water-wet to a less waterwet state with decreasing salinity (Figure 2.10). Their results disagree with that of Teklu et al. [10], who found that the contact angle increases with increasing salinity. This could be due to the effect of exposure time of CO₂ enriched brine on the oil saturated sandstone substrate. The study conducted by Seyyedi et al. [123] found that the values of the contact angle measured in the system with CO₂-enriched brine were slightly higher than those measured in the system with brine phase alone, which indicates that injection of CO₂ alters the wettability towards slightly less water-wet in quartz rock. This finding is also contradictory to the results from Teklu et al. [10] and Al-Abri et al. [107]. The difference in the findings can be ascribed to the salinity of the brine and the rock minerals used in the experiments. Therefore, it is necessary to conduct more investigations on the effect of interactions among crude oil, sandstone or pure quartz, salinity of brine, and CO₂ on wettability alteration during CO₂ LSWAG process. It is seen that injection of CO₂ and LSW could potentially result in wettability alteration, which

affects ultimate oil recovery. Additionally, initial wettability of the reservoir is also an affecting factor not only for the effectiveness of LSWI, but also for hysteresis effect during LSWAG cycles. Even though no studies have conducted so far to investigate the effect of initial wettability on hysteresis effect of CO₂ LSWAG injection, Shahverdi et al. [124] have performed investigation on relative permeability and hysteresis during WAG injection in reservoir rock with different initial wettability. Their results report that no considerable hysteresis in relative permeability was observed for water-wet cores, whereas the intermediate cores show slight cyclic hysteresis. Injection of LSW into reservoir rock that is initially intermediate-wet to oil-wet, wettability alteration could occur. When LSW is incorporated with

CO₂ WAG injection, it is possible that it could have an impact on hysteresis, which requires more investigation.

2.4.2 Simulation Studies of CO₂ LSWAG Injection

Extensive modeling works have been carried out on the WAG process. The effect of different parameters, such as WAG ratio, cycle volume, wettability [125-128], relative permeability, capillary pressure [36, 37, 126, 128-132], petrophysical properties [128, 133, 134], and miscibility [36, 37, 128, 131, 135, 136], have been investigated. However, only a few modeling [132, 137-140] studies have been conducted on LSWI, mainly due to the complex geochemical reactions in the crude-oil/brine/rock (COBR) system and lack of consensus on some of the proposed LSWI mechanisms. Generally, the dominant mechanism considered for modeling LSWI is wettability alteration achieved by interpolation between two relative permeability curves, representing high and low salinity water. The interpolants can be salinity [132], salinity of a specific aqueous component [141], equivalent fraction of a specific aqueous component on the exchanger [138] [139, 140, 142], or porosity changes induced by mineral dissolution. Fjelde et al. [137] used a 1-dimensional fully implicit black oil simulator for history matching of the water-oil relative permeability and capillary pressure curves. The curves for relative permeability and capillary pressure are estimated based on the production history and differential pressure. In order to achieve a relatively accurate model for LSWI, the two sets of relative permeability curves need to be precisely defined and geochemical reactions like intraaqueous reactions, ionic exchange, and mineral dissolution/precipitation should be incorporated into the simulator.

Preliminary modeling of the CO_2 LSWAG hybrid process was initiated by Dang et al. [7] and followed by Naderi and Simioo [103] and Nguyen et al. [143]. Dang et al. [7] first performed simulations in a 1-dimensional heterogeneous reservoir and then upscaled to a field scale. They used the model from Nghiem et al. [144] to simulate the CO_2 flooding process considering CO_2 dissolution in oil and water, and models from Dang et al. [140, 142] to simulate LSWI process taking into account of ion exchange, mineral dissolution, and wettability alteration. These proposed models have been implemented in an equation-of-state compositional simulator. Ion exchange and wettability alteration are considered to be the dominant mechanism of LSWI [7]. Wettability alteration by LSWI is modeled with relative permeability curves shifting towards more water-wet. Their results [7] confirmed the advantages of CO₂ LSWAG injection. Calcite dissolution was found to play an important role since higher oil recovery is observed with an increase in the amount of calcite. Subsequently, they extended the simulation to the field scale implementation of CO₂ LSWAG injection in the Brugge field reservoir through an integrated workflow including geological modeling, multi-phase and multi-component reservoir flow modeling, and robust optimization. One interesting observation from their results is that LSWI could potentially compensate for the delayed production caused by CO₂ injection (Figure 2.11). We consider the acceleration of oil production in the early stage is due to the effect of LSW, which promotes the ion exchange and other geochemical reactions, favorable for oil production. Naderi and Simjoo [103] adopted similar approach for modeling and investigating EOR potential of CO₂ LSWAG injection in oil-wet sandstone. Their results support the potential application of CO₂ LSWAG injection and the rate of calcite dissolution increased due to the dissolution of CO₂ into the water phase, which further promotes geochemical reactions of the rock/oil/brine/CO₂ system.



Figure 2.11 Cumulative oil recovery of different cases [7]

Subsequently, Nguyen et al. [143] modeled fines transport (fines deposition, migration, and plugging) using the approach from Gorucu et al. [145] and investigated the role of fines transport while integrating it with wettability alteration and geochemical reactions. Fines transport is considered in LSWI as follows:

$$\frac{\partial V_t}{\partial t} = \beta_1 c_f^k - \beta_2 V_{depo}^k (v_{iw} - v_{cr}) + \beta_3 (1 + \beta_4 V_t^n) v_{sw} c_f^k$$
(21)

where, β_1 , β_2 , β_3 , and β_4 are the coefficients for deposition, migration, plugging, and snow ball, respectively; v_{iw} , v_{cr} , and v_{sw} are the interfacial, critical, and superficial water velocities, respectively; V_i and V_{depo} are the volume fraction of total fines and deposited fines, respectively. Their results showed that fines transport plays an important role in LSWI. Fines migration and plugging by LSW can cause permeability reduction, potentially leading to formation damage [58, 146]. However, fines migration may also affect mobility by blocking the flow path in high permeability zones and directing the flow to unswept pores and pore throats, contributing to improved oil recovery. The simulation result shown in Figure 2.12 suggests a new way in which the hybrid EOR technique could work. In this simulation, two scenarios are modeled: (i) low-salinity (LS) water flooding (up to mid-2007) followed by CO_2 flooding (mid-2007 to 2020) and (ii) high-salinity (HS) flooding followed by CO_2 flooding. During LS water flooding, oil recovery is higher as compared to HS water flooding as a result of fines migration, wettability alteration and ion exchange. When the recovery method switches to CO_2 flooding, since fines plugging blocked the high permeability porous media, CO_2 invades low permeability zones and recovery includes previously untouched residual oil.



Figure 2.12 LSW + CO₂ flooding vs. HSW + CO₂ flooding at field scale [143] Very limited simulation work has been performed with respect to CO₂ LSWAG injection in carbonate [102, 147, 148]. Al-Shalabi et al. [149] conducted geochemical investigations using PHREEQC on the coupling effect of CO₂, low salinity water, and carbonate reservoir rock (calcite, dolomite, and anhydrite) at reservoir condition. The geochemical analysis indicates that carbonate with high dolomite composition shows the most significant effect induced by CO₂ and LSW and carbonate with high anhydrite composition are affected by only LSWI. Furthermore, Al-Shalabi et al. [147] performed numerical modeling in carbonate using a compositional and multiphase flow simulator (UTCOMP). Baker's model is used for three phase relative permeability with a modified LSWI model in carbonate [150], whereas the effects of gravity and capillary are neglected. The residual oil saturation is selected from the minimum value of oil saturation due to CO₂ injection and due to LSWI. Miscible CO₂ LSWAG

injection outperformed the other EOR methods including simultaneous WAG injection, continuous gas injection and tapered WAG injection in terms of oil recovery and CO₂ utilization factor. They highlighted that CO₂ controls the residual oil saturation and LSW boosts oil production rate through increment in oil relative permeability caused by wettability alteration. However, since this simulation package is not capable of modeling the geochemical reactions like ion exchange and mineral dissolution, the conclusion is limited.

Despite all these simulation studies trying to capture the features in a CO_2 LSWAG injection, including CO_2 dissolution and dispersion in oil and water, aqueous reactions, ion exchange, mineral dissolution/precipitation, and wettability alteration, the hysteresis effect has been ignored. The use of an accurate simulation model with hysteresis in relative permeability and capillarity contributes to better predicting the performance of CO_2 LSWAG injection. Therefore, investigating CO_2 LSWAG injection with hysteresis model, as well as history matching with experimental data could be considered for further research.

2.4.3 Proposed Mechanisms of CO₂ LSWAG Injection

The proposed mechanisms of CO₂ LSWAG injection are a combination of LSWI and CO₂ WAG injection, as summarized in Figure 2.13. Al-Abri et al. [107] proposed that the improved oil recovery by immiscible CO₂ LSWAG injection is due to mobility control and wettability alteration. The IFT between high salinity brine and oil reduces as CO₂ is introduced, however, changes in the IFT of low salinity brine and oil are not noticeable, indicating that IFT reduction is not a dominant mechanism in this process. They also suggest MIE mechanism that Na⁺ substitutes the divalent cations (Ca²⁺ and Mg²⁺), accounts for the higher oil recovery when injecting monovalent NaCl brine compared to injection of KCl and MgCl₂ brine. Teklu et al. [10] claimed that CO₂ LSWAG injection improved oil recovery of conventional CO₂ WAG injection by forming in-situ carbonated water of higher CO₂ saturation in the brine phase due to the higher CO₂ solubility in low salinity water. This in-situ carbonated water promotes wettability alteration towards more water-wet and CO₂-brine IFT reduction, hence improved oil recovery. This is similar to the mechanism proposed by Aleidan et al. [151] for CO₂ LSWAG injection in carbonate reservoir. Chaturvedi et al. [9] and AlQuraishi et al. [104] suggest that fines migration and wettability alteration, which are mechanisms for LSWI, might be the dominant mechanisms for increased oil recovery by CO₂ LSWAG injection. The presence of clay minerals, especially kaolinite, is considered essential. However, this proposed mechanism is questioned by Zolfaghari et al. [8] as they achieved oil recovery in sandstone without kaolinite. Wettability alteration towards more water-wet by CO₂ LSWAG injection is put forward by Al-Saedi et al. [105, 106, 152] as the mechanism. Moradpour et al. [153] proposed that CO₂ LSWAG injection improves oil recovery in carbonate through higher CO₂ dissolution in LSW which promotes oil mobilization by wettability alteration towards more water-wet and minimizing the contrast between oil and water density.



Figure 2.13 Proposed combined mechanisms of LSWI and CO₂ WAG injection in sandstone Based on the proposed mechanisms, wettability alteration and mobility control might be considered as the dominant mechanisms in CO₂ LSWAG injection. However, some investigations [11, 12] showed that CO₂ salted out due to increased salinity, leading to better

mobility control and LSE was not observed. This could be due to the strongly water-wet initial wettability, which is not favorable for LSW.

Simulation studies conducted on CO₂ LSWAG injection [7, 143] suggest two possible mechanisms from combining LSWI and CO₂ WAG injection:

(1) LSWI compensates the delayed production by CO₂ WAG injection in the early stage, and CO₂ WAG injection assists in promoting ion exchange and geochemical reactions for LSWI;

(2) Fines migration by LSWI increased oil recovery by plugging the high permeability porous media; hence, the absolute permeability in these layers is reduced. As CO₂ is injected into the reservoir, it is then diverted and flow with the LSW to the unswept zones with low permeability to provide additional oil recovery.

However, there is a lack of experimental evidence to validate the assumption of water blockage induced by LSW. Therefore, more detailed studies should be carried out to understand the mechanisms and conditions where CO_2 LSWAG injection will yield the highest recovery.

2.4.4 Working Conditions and Screening Criteria for CO₂ LSWAG Injection

Based on the pervious core flooding experiments, the EOR potential of CO_2 LSWAG injection is not always shown (Table 2.8). There are some general conditions which are essential for this hybrid method to work: (1) the presence of clay minerals; (2) initial wettability from intermediate-wet to oil-wet; (3) polar compounds of oil. As seen from Table 2.8, there is one case [8] showing EOR potential without clay presence. However, it is worth mentioning that heavy crude oil is used in this studying, indicating sufficient amount of polar compounds of oil. There are three cases showing no EOR potential even with clay presence. The main reason is because the initial wettability of the cores is strongly water-wet. The criteria listed might not guarantee the EOR potential of CO_2 LSWAG injection since there might be times that the dominant effect is either CO_2 or LSW. If the dominant effect is LSW, the presence of multivalent cations in formation brine should be added as one more requirement.

	6 1	0 1
Initial Wettability	Water-wet	Intermediate-wet to Oil-wet
No Clay	$Y \times 1$ [8]	/
<0.5% Clay	$Y \times 2$ [105, 107] $N \times 2$ [12, 104]	<i>Y</i> × 2 [10, 106]
2 - 6% Clay	$Y \times 2$ [9, 104] $N \times 1$ [11]	/

Table 2.8 Summary of CO₂ LSWAG injection EOR potential from core flooding experiments

Legends: Y - yes; N - no; / - no data found

2.4.5 Research Gap

The cyclic nature and the three-phase flow during WAG add additional complexities to accurately model and forecast CO₂ LSWAG performance in porous media. It is essential that the models are able to capture the saturation-direction and saturation-history dependency in three phase relative permeability and capillary pressure [154]. However, the proposed hysteresis models so far suffer from the limitation in modeling hysteresis when one phase disappears or appears due to mass transfer. In addition, using the current three phase hysteresis models for compositional simulation is complexed [154]. Even though hysteresis is more significant in non-wetting phase (gas), it may occur in wetting phase as well with up to two orders of magnitude difference in relative permeability at equivalent saturation [33]. Some experimental and simulation work investigated the effect of LSWI on capillary pressure hysteresis [155, 156], LSE is more significant when more pronounced hysteresis effect in capillary pressure is observed. This microscale hysteresis effect may be ascribed to contact angle hysteresis related to wettability and capillary dynamics and can be influenced by the surface roughness and tortuosity in the reservoir. Therefore, more research can be carried out to investigate and develop a hysteresis model in CO₂ LSWAG injection which captures the cyclic nature of CO₂ WAG process, as well as LSWI, and then incorporate the hysteresis model with the compositional geochemical simulators for proper simulation of CO₂ LSWAG injection. Moreover, the effect of wettability, ionic concentration and composition, mineral dissolution

on the hysteresis effect during CO₂ LSWAG injection might also be an open topic for investigation.

Due to the acidic effect of CO₂, CO₂ LSWAG process is likely to lower pH value compared to implementing LSWI alone [149]. The acidic effect contributes to the occurrence of mineral dissolution or precipitation, leading to changes in pore structures, surface roughness, tortuosity of flow path, and ion concentrations. These changes could further affect wettability, fines migration, and oil desorption. For carbonate reservoir or sandstone reservoir with high content of calcite cementation or anhydrite cementation, consideration of mineral dissolution and precipitation is essential. As discussed earlier, CO₂ LSWAG injection has the potential for enhancing oil recovery. However, there is so far no research conducted at pore scale and nano scale to investigate the mechanisms and effect of different parameters, as well as intermolecular forces and thermodynamics of the geochemical reactions in the oil/brine/rock/CO₂ system. Pore-scale micro-model or micro-CT experiments can assist in understanding whether clay is essential for the success of CO₂ LSWAG injection with visualization since core flooding experiments conducted by Zolfaghari et al. [8] showed LSE in CO₂ LSWAG injection in

2.5 Simulation Investigation on Hysteresis Effect

According to the research gap described in section 4.5, investigation on the hysteresis effect during CO_2 LSWAG process is void. To fill this research gap, we have carried out simulation studies of hysteresis effect on miscible CO_2 LSWAG injection.

2.5.1 Modeling of CO₂ LSWAG Injection and Hysteresis Effect

CO₂ LSWAG injection process is modeled with a compositional simulator, CMG-GEMTM, capable of capturing the geochemical and mineral reactions, as well as the wettability alteration induced by low salinity water. Modeling of these reactions and wettability alteration has been well explained in the work conducted by Dang et al. [7] and section 4.2. This simulator is also

capable of modeling the hysteresis effect with options of two-phase Land and Carlson model and three-phase Larsen and Skauge model. To investigate the effect of hysteresis model and salinity on oil recovery, two-phase and three-phase hysteresis models are incorporated into CO₂ LSWAG injection modeling. The first approach is to use the bounding drainage and imbibition curves (Stone I) along with the two-phase Carlson hysteresis model [157]. The second approach is to use the three-phase hysteresis model developed by Larsen and Skauge [129] along with Stone I relative permeability correlation. Differences in the hysteresis effects are compared in terms of oil recovery. The impact of the salinity on hysteresis effect in terms of oil recovery is also investigated.

2.5.1.1 Hysteresis Modeling

The two-phase Land and Carlson model and three-phase Larsen and Skauge model are incorporated in CMG-GEMTM simulator for modeling hysteresis effect in WAG process. This section gives a brief description of the two models.

The two-phase Land and Carlson hysteresis model [157, 158] are founded on Land's trapping model [159]. In the Land's model, gas saturation is separated into trapped gas saturation and free gas saturation. The trapped gas saturation, S_{gr} , (non-wetting phase) is computed as

$$S_{gr} = S_{gcrit} + \frac{S_{g,max} - S_{gcrit}}{1 + C(S_{g,max} - S_{gcrit})}$$
(22)

where, S_{gcrit} is critical gas saturation, $S_{g,max}$ is maximum gas saturation at the flow reversal, and C is Land's trapping parameter. The free gas saturation (S_{gf}) contributing to the flow is computed as a function of gas saturation (S_g) and trapped gas saturation as shown in Eq. (23):

$$S_{gf} = S_{gcrit} + \frac{1}{2} \left[\left(S_g - S_{gr} \right) + \sqrt{\left(S_g - S_{gr} \right)^2 + \frac{4}{C} \left(S_g - S_{gr} \right)} \right]$$
(23)

In this study, we consider the two-phase hysteresis model to follow the theory of Land and Carlson. In Carlson's model, the scanning curve is parallel to the input imbibition curve and can only be applied to the non-wetting (gas) phase as shown in Figure 2.14. The solid curves are the gas relative permeability input for the imbibition and drainage processes obtained from laboratory experiment. The gas relative permeability on the drainage to imbibition scanning curve, the dashed line for instance (Figure 2.14), is computed with Eq. (24):

$$K_{rg}^{imb}(S_g) = K_{rg}^{drain}(S_{gf})$$
⁽²⁴⁾

where, K_{rg}^{imb} is the gas relative permeability on the imbibition curve and K_{rg}^{drain} is the gas relative permeability on the drainage curve.



Figure 2.14 Carlson hysteresis model on the non-wetting gas phase

The three-phase hysteresis model implemented in this study is based on the model from Larsen and Skauge [129]. The primary gas relative permeability curve is used together with Land's model to generate scanning curves. If the gas saturation decreases once again, a secondary drainage curve will be generated as follows:

$$K_{rg}^{drain} = \left[K_{rg}^{input} - K_{rg}^{input}(S_g^{start})\right] \left[\frac{S_{wcon}}{S_w^{start}}\right]^{\alpha} + \left[K_{rg}^{imb}(S_g^{start})\right]$$
(25)

where, K_{rg}^{input} is the input gas relative permeability, $K_{rg}^{input}(S_g^{start})$ is the input gas relative permeability at the start of the secondary drainage, S_{wcon} is the connate water saturation, S_w^{start} is the water saturation at the start of the secondary drainage, $K_{rg}^{imb}(S_g^{start})$ is the gas relative permeability at the start of the secondary drainage, and α is the gas relative permeability reduction factor.

For the three-phase scenario, there would be significant reduction in water mobility compared to its original mobility in the oil/water system after the injection of gas, [126]. Therefore, for an imbibition process with increasing water saturation, interpolation is carried out between the two-phase and three-phase inputs (Figure 2.15) with Eq. (26) to calculate the imbibition relative permeability (K_{rw}^{imb}):

$$K_{rw}^{imb} = K_{rw}^{W2} \left(1 - \frac{S_g^I}{S_{g,max}} \right) + K_{rw}^{W3} \left(\frac{S_g^I}{S_{g,max}} \right)$$
(26)

where, K_{rw}^{W2} is the water relative permeability from the two-phase curve, K_{rw}^{W3} is from the three-phase curve, and S_g^I is the gas saturation in the beginning of the imbibition process.



Figure 2.15 2-Phase and 3-Phase relative permeability input for the Larsen and Skauge model

2.5.1.2 Core-Scale Model and LSWI Description

A composite core-scale model (Figure 2.16) with properties shown in Table 2.9 is built for this simulation study. The initial water saturation is equal to connate water saturation, 0.03. The

API oil gravity is 32. The WAG ratio is set to be 1:1 as most of the experimental results show that this WAG ratio delivers the best performance in terms of oil recovery [5].



Figure 2.16 Composite core-scale model

Table 2.9 Pro	perties and o	perational	parameters	of the	core-scale	model

Parameter	Value
Grid block system	100 x 1 x 1
Grid block sizes	$\Delta x = 0.312$ cm, $\Delta y = 3.345$ cm, $\Delta z = 3.345$ cm
Porosity	17x0.1845 17x0.1845 17x0.1859 17x0.1862 17x0.1835
	15x0.1846
Permeability (mD)	17x2412 17x2235 17x2280 17x2285 17x2180 15x2240
Initial water saturation	0.03
Reservoir temperature	100°C
Initial reservoir pressure	42,446 kPa (6156 psi)
Injection rate	$11 \text{ cm}^{3}/\text{h}$
WAG ratio	1:1
Total pore volume injected	2
Equation of state	Soave-Redlich-Kwong
Bubble point	37,335 kPa (5414 psi)
Oil API gravity	32
Formation volume factor	1.68 rm ³ /sm ³

Figure 2.17 shows the relative permeability curves obtained from experimental data representing high and low salinity water. These two sets of curves are used for interpolation to model wettability alteration by LSWI. The relative permeability curves for high salinity water

represent a more oil-wet condition, and those for low salinity water represent a more water-wet condition. Low salinity effect is modeled with a shift in the relative permeability curves from oil-wet to water-wet. Equivalent fraction of Na⁺ on the negatively charged surface is used as interpolant for relative permeability interpolation. The composition of formation water initially present in the reservoir is listed in Table 2.10, which is used as input for the core-scale model. The compositions of the low salinity water and seawater in the water injection cycles are shown in Table 2.10. The salinity of the low salinity water is chosen to be 2000 ppm, which is within the salinity range for LSWI [59].



Figure 2.17 Relative permeability for high and low salinity water

Table 2.10 Composition of formation and injection water					
Component	Formation Water	Seawater	Low Salinity Water		
Na ⁺ , mg/L	35,671	10,974	614		
Mg ²⁺ , mg/L	330	1,310	73		
Ca ²⁺ , mg/L	3,599	420	23		
K ⁺ , mg/L	225	407	23		
Cl ⁻ , mg/L	62,371	19,740	1,104		
SO4 ²⁻ , mg/L	233	2,766	155		
HCO ₃ ⁻ , mg/L	-	129	7		
Total	102,430	35,746	2,000		

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Table	<i>i</i> 10	('omi	nocition	Δt	tormation	nond	111	100t10n	wotor
I a U I C Z	2.10	COIIII	JUSILIUH	UI.	TOTHIALIOI	i anu		ICCHOIL	water

2.5.1.3 Modeling Investigation Approach

With the core-scale model, LSWI and hysteresis modeling in place, investigation on hysteresis effect on CO₂ LS WAG and seawater WAG (SWAG) injection is evaluated through two-phase Land and Carlson model and three-phase Larsen and Skauge model using Stone I relative permeability correlation [129]. The main input for the Land and Carlson model is the bounding drainage curve and Land parameter, and for Larsen and Skauge model is primary drainage curve, Land parameter, and gas relative permeability reduction factor.

The effect of hysteresis model on oil recovery is investigated with Land parameter of 0.8 as recommended by Egermann et al. [133] and gas relative permeability reduction factor of 3.32 as suggested by Hosseini et al. [160]. The effect of salinity on three-phase hysteresis is also investigated with varying salinities (2000, 5000, 10000, 20000, 35746 ppm). All these cases are conducted with WAG ratio of 1:1 and are simulated as secondary recovery mode. Capillary pressure is ignored in this study.

2.5.2 Results and Discussion

This section presents the results from the core-scale simulation and the discussion on the effect of hysteresis model and salinity on CO₂ WAG injection process.

2.5.2.1 Effect of Hysteresis Model on Oil Recovery

Table 2.11 summarizes the oil recovery factor with and without hysteresis for CO₂ LSWAG injection (2000 ppm low salinity water) and CO₂ WAG injection (35746 ppm seawater). The two base cases are the CO₂ LSWAG and WAG injection with no hysteresis.

Case	Recovery scheme	Hysteresis model	Land parameter	Gas reduction factor	Recovery Factor	% Difference from base case
#1	CO	None	N/A	N/A	85.4%	Base 1
#2	UO_2	2 Phase	0.8	N/A	85.4%	0%
#3	WAG	3 Phase	0.8	3.32	85.7%	0.35%
#4	COLS	None	N/A	N/A	86.6%	Base 2
#5	$U_2 LS$	2 Phase	0.8	N/A	86.1%	-0.8%
#6	WAU	3 Phase	0.8	3.32	86.1%	-0.8%

 Table 2.11 Summary of simulation results

It is observed from Table 2.11 that the differences in oil recovery factor due to hysteresis is not significant. It is worth noting that there is a slight increase in recovery factor with 3-Phase hysteresis in CO_2 WAG injection (#1 and #3), however, the opposite trend is observed for CO_2 LS WAG injection (#4 and #6). Comparing the differences of 2-Phase Carlson and 3-Phase Larsen and Skauge model in CO_2 WAG injection (#1, #2, and #3), 2-Phase model has no effect on oil recovery, whereas a slight increase is observed with 3-Phase model. With CO_2 LS WAG injection (#4, #5 and #6), applying 2-Phase and 3-Phase model makes no difference.

Despite the negligible differences in oil recovery due to hysteresis effect, different changing trend is seen for injection water with different salinities (2000 ppm and 35746 ppm). This indicates that salinity of the injection water might also play a role in cyclic WAG injection process, which is further discussed in the next section.

2.5.2.2 Effect of Salinity

The effect of salinity is investigated through varying injection water salinities from 2000 ppm to 35746 ppm (seawater) in the CO₂ WAG process (2000 ppm, 5000 ppm, 10000 ppm, 20000 ppm, and 35746 ppm). Figure 2.18 shows the results with oil recoveries plotted against salinities.



Figure 2.18 Oil recovery factor for CO₂ WAG injection hysteresis simulations with different salinities

Even though changes in oil recovery with respect to salinity is relatively small in this corescale simulation, the changing trend is worth mentioning since the effect might be magnified in the field scale. From Figure 2.18, oil recovery of CO₂ WAG injection with no hysteresis remains unchanged from 35746 ppm to 10000 ppm and increases with decreasing salinity from 10000 ppm to 2000 ppm due to low salinity effect. However, with 2-Phase and 3-Phase hysteresis models, the changing trend of oil recovery varies in the range of 2000 ppm to 10000 ppm. Instead of a constant increase in oil recovery from 10000 ppm to 2000 ppm, oil recovery slightly increases to a peak from 10000 ppm to 5000 ppm and decreases from 5000 ppm to 2000 ppm. Could this be caused by the differences in LSE with different salinities?

Figure 2.19 shows that oil recovery by only water injection increases from 100000 ppm to 2000 ppm. Thus, the trend changing in oil recovery of CO_2 WAG injection might be mainly due to the hysteresis effect. CO_2 LSWAG injection with 5000 ppm salinity in injection water results in the highest oil recovery compared to 2000 ppm salinity, even though injecting 2000 ppm water achieves the highest in LSWI (Figure 2.19).



Figure 2.19 Oil recovery by water injection with varying salinities

It can be inferred from the simulation results that it is more accurate to include the effect of hysteresis in CO₂ LSWAG injection modeling and optimization. Neglecting the hysteresis effect might not lead to significant error in core-scale simulation. However, if the modeling and optimization are performed at reservoir scale, excluding hysteresis could result in choosing wrong operational parameters and salinities.

2.6 Conclusions

This paper presents a review of the effect of different parameters on CO_2 LSWAG injection, and the independent and combined mechanisms of LSWI and CO_2 WAG injection. A simulation investigation on the hysteresis effect in CO_2 LSWAG injection has been conducted to fill the identified research gap. The following are the conclusions and recommendations based on this literature review and simulation study:

(1) The EOR potential of CO₂ LSWAG injection has been confirmed by laboratory experiments and simulation studies. Initial wettability, the composition and salinity of injection and formation brine, WAG parameters, and reservoir pressure and temperature determine the success of this method;

- (2) Laboratory experiments suggest that mobility control and wettability alteration (towards more water-wet) could be the dominant mechanisms for CO₂ LSWAG injection;
- (3) Simulation studies proposed two effects for CO₂ LSWAG injection. One is that LSWI could potentially compensate for the delayed production by CO₂ WAG injection in the early stage, and the injection of CO₂ promotes ion exchange and geochemical reactions for LSWI due to its reaction with water and calcite minerals. The other one is that fines migration, and subsequent water blockage induced by fines plugging, divert the flow path to unswept low permeability zones. Due to the lack of experimental evidence, more laboratory experiments, especially pore-scale studies, are recommended to investigate the driving forces and mechanisms for improved oil recovery by CO₂ LSWAG injection;
- (4) There is no consensus as to which mechanisms are dominant in improving oil recovery during LSWI, and limited research on the interactions between CO₂, crude oil, brine and reservoir rocks. Hence, extensive laboratory studies and simulations on a field scale should be conducted prior to any field-scale application of CO₂ LS WAG injection;
- (5) Development of a more reliable CO₂ LSWAG injection model is necessary, considering geochemical interactions of the crude oil/brine/rock, three-phase relative permeability, capillary pressure, and hysteresis effect;
- (6) Further investigations are required to thoroughly understand the effect of interactions between crude oil, low salinity water, rock minerals and CO₂ on wettability modification during CO₂ LSWAG injection;
- (7) Despite the existing challenges, this hybrid technique has the potential to improve oil recovery at low cost in both offshore and onshore reservoirs with ongoing or planned water flooding and CO₂ WAG injection projects; and
- (8) Our simulation investigation on the hysteresis effect indicates that it is more accurate to

include hysteresis in CO2 LSWAG injection modeling and optimization. Even though the hysteresis effect is not significant at core scale, excluding it at reservoir scale might lead to large errors in oil recovery prediction as well as operational parameters and salinity optimization. Moreover, more laboratory data with respect to the imbibition and drainage curves considering different salinities is also required to better model the CO₂ LSWAG injection process.

2.7 Nomenclature

Acronyms	
API	American Petroleum Institute
BHP	Bottom hole pressure
Ca^{2+}	Calcium ion
CaCl ₂	Calcium chloride
Cl-	Chloride ion
CMG	Computer Modeling Group
CO_2	Carbon dioxide
COBR	Crude-oil/brine/rock
DECE	Designed exploration controlled evolution
EOR	Enhanced Oil Recovery
GA	Genetic algorithm
HCO ₃ -	Bicarbonate ion
H_2CO_3	Carbonic acid
HS	High salinity
HSW	High salinity water
IFT	Interfacial tension
LPG	Liquified petroleum gases
LS	Low salinity
LSE	Low salinity effect
LSW	Low salinity water
LSWAG	Low salinity water-alternating-gas
LSWI	Low salinity water injection
K^+	Potassium ion
KCl	Potassium chloride
K _{rg}	Gas relative permeability
Na^+	Sodium ion
NaCl	Sodium chloride
Na_2SO_4	Sodium sulfate
md	Milli Darcy
Mg^{2+}	Magnesium ion
MgCl ₂	Magnesium chloride
MIE	Multi-component ionic exchange
MMP	Minimum miscible pressure
MSW	Modified seawater

Net present value
Original oil in place
Parts per million
Particle swarm optimization
Pore volume
Response surface methodology
Sulfate ion
Total dissolved solids
Compositional and multiphase flow simulator
Water-alternating-gas
Wettability index
Without NaCl
Without NaCl and 5-time diluted Ca ²⁺
Without NaCl and 5-time diluted Mg ²⁺
Without NaCl and 5-time diluted SO ₄ ²⁻

Variables and parameters

Μ	Mobility ratio
Sg	Gas saturation
S _{gcrit}	Critical gas saturation
$S_{ m gf}$	Free gas saturation
S _{g,max}	Maximum gas saturation at the flow reversal
S _{gr}	Trapped gas saturation
S_w	Water saturation
V	Volume fraction

Greek letters

ζ	Zeta potential
λ	Mobility
θ	Contact angle
β	Coefficient
ν	Velocity

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Chapter 3 Low Salinity Water Injection Modeling: Investigating Relative Permeability Interpolation Techniques

This chapter investigates the effect of different relative permeability interpolation techniques and temperature on oil recovery, pH changes, and mineral dissolution/precipitation in LSWI modeling. It is ready for submission.

Abstract

Low salinity water injection (LSWI) is a promising enhanced oil recovery (EOR) method with many advantages from both an economic and environmental perspective. This paper is based on the widely agreed working mechanism that wettability alteration from oil-wet to water-wet is responsible for the improved oil recovery by LSWI. Previous studies have investigated LSWI using salinity or equivalent fraction of an aqueous component on the exchanger as interpolants for relative permeability interpolation, however, using porosity/permeability increase induced by mineral dissolution as an interpolant is not reported. Thus, increase in porosity and subsequent permeability is introduced as an interpolant in this work and is studied along with interpolants such as Na⁺ concentration and equivalent fraction of Na-X. Moreover, even though the temperature effect on LSWI has been evaluated through core flooding experiments, no modeling work has been found to investigate the effect of injection temperature on low salinity effect and its related impact on oil recovery, pH distribution, and mineral reactions. The focus of this paper is to investigate and compare the different relative permeability interpolation techniques and important aspects such as oil recovery, changes in pH, and mineral dissolution/precipitation due to LSWI, and the effect of temperature in the reaction process, particularly in the near-well region. Oil recovery factor is found to be affected by different interpolation technique, as well as pH and temperature of the injection water. Low injection temperature reduces the low salinity effect. There is no clear relationship between oil recovery factor and pH increase. Bicarbonate ions are found to have an influence on pH. With the effect of temperature, bicarbonate ions act as buffer for pH changes as low salinity water is injected into the reservoir block model. Calcite dissolution and dolomite precipitation occur during LSWI near the injector.

Keywords: Low Salinity Water Injection (LSWI), Precipitation and Dissolution, Temperature Effect, Oil Recovery Factor

3.1 Introduction

Water flooding is the most commonly used technique for secondary oil recovery to improve sweep efficiency, due to its availability and low cost. Bernard [1] first introduced salinity as a variable that could influence the efficiency of water flooding in formations containing hydratable clays. It was found that as the concentration of injected sodium chloride brine was lowered from 1% to 0.1%, oil recovery increased. This low salinity effect (LSE) in sandstone encouraged more researchers and companies such as British Petroleum (BP) [2-4], ExxonMobil [5], TOTAL [6, 7], Shell [8-12], Equinor [13, 14] and Schlumberger [15, 16] to investigate the effect of low salinity water injection (LSWI). Mechanisms such as fines migration [17, 18], increased pH and IFT reduction [19, 20], osmotic pressure [21-25], salt-in effect [26], multi-component ion exchange (MIE) [27, 28], expansion of electrical double layer [8, 29], mineral dissolution [30], and wettability alteration [12, 31, 32] have been proposed in the past decades. Due to the complexity of the oil/rock/brine systems, LSE might be an interplay of several mechanisms [33]. Modeling of LSWI is dependent on the assumption of the working mechanisms. Generally, wettability alteration is modeled with a shift in relative permeability curves [34], fines migration is modeled with decline in permeability induced by fines release, migration, and plugging [35]. Geochemical processes like MIE and pH changes induced by LSWI have been modeled with Phreeqc [36, 37], which is a geochemical reaction package capable of simulating geochemical reactions including ion exchange, equilibrium, surface complexation and etc.

Jerauld et al. [38] proposed an analytical model relating relative permeability and capillary pressure directly to salinity and considering salt as an additional single lumped component. The interpolant is calculated as the dependence of residual oil on salinity between high and low salinity waters. In their model, ion exchange between the rock surface, monovalent and multivalent cations was not considered. As LSWI is a geochemical process coupled with multi-

phase flow along the flowing path in the reservoir, modeling the LSWI process requires the simulator to well capture the geochemical reactions in the oil/brine/rock systems. Similar linear dependence of residual oil on salinity was employed by Fjelde et al. [34], but considering ion exchange in a 1-dimensional fully implicit black oil simulator. Omekeh et al. [39] proposed a model in which the interpolant is the divalent cation released from the rock surface. Although their model matches the experimental two-phase core flooding data in terms of ion composition and pH, it would be better to use a compositional model with full geochemical reactions, rather than a simplified two-phase flow model. Korrani et al. [40] developed geochemical-based modeling of LSWI by coupling UTCOMP reservoir simulator [41] with Phreeqc [37]. Three interpolation techniques are implemented. One is using the total ionic strength as the interpolant with the assumption that the dominant mechanism is expansion of electrical double layer, and the other two interpolants are fraction of the organometallic complexes on the exchanger and changes in moles of the organic oil component in the surface complex assuming MIE is the dominant mechanism. Dang et al. [42-44] developed a compositional and geochemical model with CMG-GEMTM for LSWI in sandstone considering wettability alteration as dominant mechanism and coupled with MIE. They used the equivalent fraction of Na⁺ and Ca²⁺ on the rock surface (Na-X or Ca-X₂) as interpolants. With the same model, Esene et al. [45] used the concentration of Na^+ (sandstone) or SO_4^{2-} (carbonate) in the aqueous phase as interpolants. Khorsandi et al. [46] used their in-house compositional simulator, Penn Sim, to simulate LSWI in sandstone reservoirs assuming wettability is the dominant mechanism and MIE affects surface wettability. Linear interpolation of the relative permeability curves is performed following Dang et al. [42]. Concentration of the adsorbed Na⁺ on the rock surface is used as interpolant which controls the wettability alteration. To summarize, there have been significant advances in modeling LSWI in sandstone reservoirs from analytical model considering salt as a single lumped component to compositional simulators coupling multiphase flow with geochemical reactions. Overall salinity, salinity of an aqueous component, and equivalent fraction of an aqueous component on the exchanger have been used as the interpolation parameters which controls the wettability alteration. As suggested by Lebedeva et al. [47] and Pu et al. [30], mineral dissolution (i.e., calcite, dolomite or anhydrate) induced by LSWI might affect brine compositions and induce secondary pore structure, which contributes to ion exchange and increased oil recovery. Thus, despite the previous mechanistic assumptions that wettability alteration is controlled by salinity decrease, equivalent fraction of Na⁺ or Ca²⁺ on the exchanger, porosity/permeability increase due to LSWI could also affect the wettability alteration and can be used as an interpolant for relative permeability interpolation to model wettability alteration. However, the use of porosity increase as interpolation parameter and how different interpolation techniques in LSWI modeling influence oil recovery, pH, and geochemical reactions have not been reported up to date. In this paper, we introduce a new interpolation technique by assuming that porosity increases are induced by mineral dissolution during LSWI, and relative permeability interpolations are carried out in terms of the porosity increase, salinity decrease, and equivalent fraction of an aqueous component on the exchanger. A compositional simulator, CMG-GEMTM, is used to model the LSWI process in sandstone reservoirs. By using different interpolants for modeling wettability alteration, their impact on the ultimate oil recovery, pH, and mineral dissolution/precipitation near the near-well region of the injector is evaluated and compared. Besides the influence of different interpolation techniques for relative permeability to model wettability alteration, temperature of the injection water could also have an impact on oil recovery, pH, and the mineral reactions. Tang and Morrow [48] conducted LSWI core flooding experiments with Berea sandstones, showing that water-wetness and oil recovery increase with temperature from 22°C to 50°C, and 75°C. Similar results were reported by Agbalaka et al. [49] on Berea sandstone core flooding experiments, of which high temperature of 218°C resulted in lower final residual oil saturation than low temperature of 13°C. However, increasing temperature might not always lead to higher oil recovery. RezaeiDoust et al. [50] found that temperature has no effect on oil recovery for the cores aged at temperature of 90°C. Aghaeifar et al. [51] conducted core flooding experiments on sandstone at reservoir temperature higher than 100°C. Their results showed no LSE. Both increase and no increase in oil recovery were reported with increasing temperature in sandstone core flooding experiments. Fu [52] has performed simulation investigation using compositional simulator, UTCOMP-IPhreeqc to investigate the effect of temperature on low salinity water injection in sandstone and carbonate, using salinity and amount of calcite as interpolation parameters respectively. No significant increase in oil recovery was found for the sandstone cases with temperature changing from 30°C to 120°C. However, oil recovery increases were observed for the carbonate cases with temperature increasing from 120°C to 150°C. It was suggested in this modeling study that low salinity might not be effective if no changes in ionic strength and viscosity ratio occur with increasing temperature and the low salinity effect observed in the carbonate cases was supposed to be due to the dissolution of calcite. However, owing the observation of no low salinity effect to no changes in total ionic strength leading to no expansion of electric double layer might not be correct. Thus, more modeling work is required to understand the temperature effect on oil recovery with its related impact on pH as well as mineral dissolution and precipitation.

Therefore, the objective of this paper is to investigate the effect of different interpolation techniques to relative permeability curves and temperature on LSWI in a sandstone block model. In our study, the temperature effect is focused on the temperature of the injection fluid. The interpolation techniques include using interpolation parameters of Na⁺ concentration, equivalent fraction of Na-X on the exchanger, and porosity increase induced by mineral dissolution. Comparisons of the three relative permeability interpolation techniques, injection

temperature and their relevant phenomena, such as improvement in recovery factor, changes in pH, mineral dissolution/precipitation around the near well region are made.

3.2 Theoretical Analysis and Modeling Approach

A compositional simulator, CMG-GEM, is used to model LSWI assuming that wettability alteration is the dominant LSWI mechanisms, and is coupled with multi-component ion exchange (MIE) [44]. This simulator has been validated with North Sea and Texas sandstone core flooding experiments [34, 53] and geochemical software PHREEQC by Dang et al. [44]. Geochemical, wettability alteration, and thermal effect modeling are discussed in this section.

3.2.1 Geochemistry and Modeling

Aqueous reactions. The aqueous reactions involve ions and species in the aqueous phase. The following Eq. (1) and (2) are two typical aqueous reactions in an oil and gas reservoir since CO₂ and water are always present [44].

$$CO_2(aq) + H_20 \rightleftharpoons H^+ + HCO_3^- \tag{1}$$

$$H_2 0 \rightleftharpoons H^+ + 0H^- \tag{2}$$

Chemical constants are used to model the equilibrium of these reactions [54] and Eq. (3) defines the chemical constant for Eq. (2) [55].

$$K_{eq} = \frac{\alpha_{H^+} * \alpha_{OH^-}}{\alpha_{H_2O}} = \frac{[\gamma_{H^+} * m_{H^+}] * [\gamma_{OH^-} * m_{OH^-}]}{\gamma_{H_2O} * m_{H_2O}}$$
(3)

where, K_{eq} is the equilibrium constant, α_i refers to the activity, γ_i is the activity coefficient, and m_i represents the molality of component *i*. Activity is related to molarity through $\alpha_i = \gamma_i * m_i$. For ideal solution, γ_i is equal to 1 and α_i is equal to the molality. However, the solution is non-ideal in most cases and activity coefficient in this modeling work is calculated using B-dot model [54, 56] in Eq. (4).

$$\log_{\gamma_i} = -\frac{A_{\gamma} * Z_i^2 \sqrt{I}}{I + \dot{a}_i B_{\gamma} \sqrt{I}} + \dot{B}I$$
(4)

where, A_{γ} , B_{γ} and \dot{B} are temperature dependent parameters, \dot{a}_i is the ion size parameter, and Z_i is the charge of the ith ion in the electrolyte. *I* is the ionic strength given by Eq. (5) [57].

$$I = \frac{1}{2} \sum_{i} m_i Z_i^2 \tag{5}$$

Multi-component ionic exchange. In a sandstone reservoir initially filled with formation water, the rock surface is saturated with multivalent cations (Ca^{2+} or Mg^{2+}) due to their higher affinity to the negatively charged clay surfaces [58] as shown in Figure 3.1. As oil enters the reservoir, some organic oil polar compounds are adsorbed directly onto the rock surface by displacing the most labile cations, and some of them are attached to the surface through multivalent cations, forming organo-metallic complexes, promoting oil-wetness of the rock [27]. With the injection of low salinity water, of which the salinity is significant lower than initial formation water, the organic polar compounds of oil and organo-metallic complexes are replaced by uncomplexed cations (i.e. Na^+) due to the effect of MIE, resulting in a more water-wet mineral surface [27].



Figure 3.1 Schematic diagram of the MIE process

Two typical MIE reactions involving Na^+ , Ca^{2+} and Mg^{2+} are shown in Eq. (6) and (7) [44].

$$\frac{1}{2}Ca - X_2 + Na^+ \rightleftharpoons \frac{1}{2}Ca^{2+} + Na - X \tag{6}$$

$$\frac{1}{2}Mg - X_2 + Na^+ \rightleftharpoons \frac{1}{2}Mg^{2+} + Na - X$$
 (7)

where, X denotes the cation exchangeable site, i.e., clay mineral surface, and Na - X, $Ca - X_2$, and $Mg - X_2$ are the equivalent fractions of Na⁺, Ca²⁺ and Mg²⁺ on the exchanger (X). The two reactions above (Eq. 6 and 7) are reversible. With the injection of low salinity water, reactions move in the right direction, resulting in a release of Ca²⁺ and Mg²⁺ ions. Na⁺ is then adsorbed onto the negatively charged clay surfaces, promoting water-wetness.

Similar to aqueous chemical reactions, MIE reactions can also be characterized with equilibrium chemical constants as shown in Eq. (8) and (9) [55].

$$K_{Na/Ca} = \frac{(\alpha_{Ca^{2+}})^{0.5} * \alpha_{Na-X}}{\alpha_{Na^{+}} * (\alpha_{Ca-X})^{0.5}}$$

$$= \frac{(m_{Ca^{2+}})^{0.5} * m_{Na-X}}{m_{Na^{+}} * (m_{Ca-X_{2}})^{0.5}} * \frac{(\gamma_{Ca^{2+}})^{0.5} * \gamma_{Na-X}}{\gamma_{Na^{+}} * (\gamma_{Ca-X_{2}})^{0.5}}$$

$$K_{Na/Mg} = \frac{(\alpha_{Mg^{2+}})^{0.5} * \alpha_{Na-X}}{\alpha_{Na^{+}} * (\alpha_{Mg-X})^{0.5}}$$

$$= \frac{(m_{Mg^{2+}})^{0.5} * m_{Na-X}}{m_{Na^{+}} * (m_{Mg-X_{2}})^{0.5}} * \frac{(\gamma_{Mg^{2+}})^{0.5} * \gamma_{Na-X}}{\gamma_{Na^{+}} * (\gamma_{Mg-X_{2}})^{0.5}}$$
(9)

The activity coefficient of Na⁺, Ca²⁺ and Mg²⁺ in the aqueous phase can be assumed to be 1 (i.e., activity equals molality), or it can be calculated by Debye-Huckel model or B-dot model [54]. However, calculation of the activity coefficient of Na - X, $Ca - X_2$, and $Mg - X_2$ is difficult. Thus, for some of the ionic exchange reactions, the selectivity coefficient defined in Eq. (10) and (11) is used instead of equilibrium constant [59].

$$\kappa_{Na/Ca}' = \frac{(m_{Ca^{2+}})^{0.5} * \zeta_{Na-X}}{m_{Na^{+}} * (\zeta_{Ca-X_{2}})^{0.5}} * \frac{(\gamma_{Ca^{2+}})^{0.5}}{\gamma_{Na^{+}}}$$
(10)

$$\kappa_{Na/Mg}' = \frac{(m_{Mg^{2+}})^{0.5} * \zeta_{Na-X}}{m_{Na^{+}} * (\zeta_{Mg-X_{2}})^{0.5}} * \frac{(\gamma_{Mg^{2+}})^{0.5}}{\gamma_{Na^{+}}}$$
(11)

where, ζ_{Na-X} , ζ_{Ca-X_2} , and ζ_{Mg-X_2} are the equivalent fractions of Na^+ , Ca^{2+} , and Mg^{2+} and m_i and γ_i are the molality and activity coefficient of component *i*. It is worth mentioning that selectivity coefficient is an operational parameter, rather than a thermodynamic variable like equilibrium constant. $\kappa'_{Na/Ca}$ and $\kappa'_{Na/Mg}$ are generally estimations from experimental measurements and are functions of temperature. Appelo and Postma [59] report selectivity coefficients between Na⁺ and other ions that are used in the CMG-GEM simulator.

Another property of exchanger is cation exchange capacity (CEC), which indicates the total capacity of the surface to hold exchangeable cations. For a given value of CEC in the grid block of CMG-GEM, Eq. (12) needs to be satisfied.

$$VN_{Na-X} + 2VN_{Ca-X_2} + 2VN_{Mg-X_2} = V\phi(CEC)$$
(12)

where, V is the grid block bulk volume, N_{Na-X} , N_{Ca-X_2} and N_{Mg-X_2} are moles of Na - X, $Ca - X_2$, and $Mg - X_2$ per grid block bulk volume, ϕ refers to porosity.

Mineral dissolution and precipitation. Mineral dissolution and precipitation can have an impact on ion exchange. According to Bethke [54], the reaction rate of dissolution and precipitation for mineral β can be expressed as

$$r_{\beta} = A_{\beta}k_{\beta}(1 - \frac{Q_{\beta}}{K_{eq,\beta}}) \tag{13}$$

where, r_{β} is the reaction rate of mineral β , A_{β} is the reactive surface area, k_{β} is the rate constant of mineral β reaction, Q_{β} is the activity product of mineral β reaction, and $K_{eq,\beta}$ is the chemical equilibrium constant for mineral β reaction. Taking calcite dissolution/precipitation (Eq.(14)) as an example, the activity product $Q_{calcite}$ can be calculated as shown in Eq.(15).

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons Calcite \tag{14}$$

$$Q_{Calcite} = \frac{1}{\alpha(Ca^{2+}) * \alpha(CO_3^{2-})}$$
(15)

The activity of calcite is not included in the activity product as it holds a value equal to 1, which is the same case for other minerals. The equilibrium constant for minerals can generally be found from literature [60]. To determine whether dissolution or precipitation occurs, saturation index, which is defined as the ratio of activity product and equilibrium constant $(Q_{\beta}/K_{eq,\beta})$, is used. If $Q_{\beta}/K_{eq,\beta} > 1$, mineral dissolution occurs and if $Q_{\beta}/K_{eq,\beta} < 1$, mineral precipitation occurs.

The rate of dissolution and precipitation in Eq. (13) applies to the mineral, whereas the formation or consumption of different species in the aqueous phase can be obtained by Eq. (16).

$$r_{k\beta} = \nu_{k\beta} * r_{\beta} \tag{16}$$

where, $r_{k\beta}$ is the reaction rate of formation or consumption of aqueous species and $v_{k\beta}$ is the reaction stoichiometry coefficient, which is an absolute value.

Generally, the reaction rate constant k_{β} varies with temperature. Eq. (16) is used to calculate the rate constant at temperature T [55].

$$k_{\beta} = k_{0\beta} * \exp\left[-\frac{E_{\alpha\beta}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$
(17)

where, $E_{\alpha\beta}$ is the activation energy, T_0 is a reference temperature, which is normally 25°C, and $k_{0\beta}$ is reaction rate constant at T_0 .

3.2.2 Wettability Alteration Modeling and Interpolation Technique

Wettability alteration by LSWI is modeled with a shift in the relative permeability curves from oil-wet towards more water-wet as shown in Figure 3.2. Typically, two sets of relative permeability curves corresponding to high and low salinity conditions are defined, which are normally obtained from experimental data and serve as the input for simulation. Each set of the curves represents one value of a specified interpolant, shown as interpolant value 1 and 2 in Figure 3.2.



Figure 3.2 Schematic diagram of wettability alteration modeling with a shift in relative permeability (adapted after Dang et al. [44])

The interpolation area is between the interpolant value 1 and 2 (Figure 3.3), which corresponds to an upper and lower bond suggesting where low salinity effect starts and ends. Generally, the interpolant value 1 and 2 are the inputs and vary with the use of interpolation techniques.



Figure 3.3 Illustration of interpolation between the input interpolant valueLinear interpolations between the two defined relative permeability curves and input interpolant values are performed through the following equation:

$$k_r = WF * k_r(j) + (1 - WF) * k_r(j+1)$$
(18)

where, $k_r(j)$ and $k_r(j+1)$ correspond to the relative permeability of the two defined datasets, k_r is the relative permeability obtained from interpolation, and WF is the distance weighting factor within the range of 0 to 1.

In this paper, the interpolation is achieved with three different approaches: simple interpolation, ion exchange interpolation, and mineral volume fraction interpolation. With simple interpolation, residual oil saturation is dependent on the concentration of the selected aqueous component in the injection brine, in terms of the equivalent ionic fraction on the rock surface, and in terms of porosity changes due to mineral dissolution.

Simple interpolation. This is the simplest interpolation method, in which the concentration of a certain aqueous component is used. Generally, the start and end of interpolation is defined in terms of the selected ion concentration. The beginning value (upper bound) of the relative permeability interpolation is the molality of the aqueous component for the case where there is no LSE. The value for the end of interpolation (lower bound) is where the strongest LSE is achieved. Relative permeability interpolation is carried out within the upper and lower bound of the selected ion concentration.

Ion exchange interpolation. By using the ion exchange interpolation, the interpolant is the equivalent fraction of cation on the negatively charged exchanger. The beginning of relative permeability interpolation is the ion exchange value where no LSE exists. The end of interpolation is the ion exchange value with the strongest LSE.

Mineral volume fraction interpolation. Mineral volume fraction interpolation of the relative permeability curves is implemented in scenario where porosity increase induced by mineral dissolution is considered as the interpolant. The value set for the beginning of relative permeability interpolation is the porosity change with no LSE. The ending value for interpolation is the porosity change with the strongest LSE.

3.2.3 Thermal Effect and Modeling

When the temperature of the injection fluid is at a different temperature than the one prevailing in the reservoir, it is necessary to evaluate the temperature profile across the reservoir and its effect on oil recovery and other phenomena such as mineral dissolution/precipitation. The thermal effect is modeled by solving the volume constraint equation, component flow equations, energy balance equation, and phase equilibrium equations. The details of the equations can be found in Appendix.

3.3 Fluid and Reservoir Modeling

This section describes the workflow for modeling of the reservoir fluid and LSWI in a block model with three approaches to relative permeability interpolation at injection temperature of 20°C and 100°C.

3.3.1 Fluid Modeling

CMG-Winprop is used to develop the fluid model of the offshore Newfoundland oil with an API gravity of 32 at standard condition. An initial EOS (equation of state) fluid model is generated using the Soave-Redlich-Kwong (SRK) equation of state. Laboratory experiments such as differential liberation (DL), constant composition expansion (CCE), and separator tests are conducted. Following the fluid modeling flow chart Figure 3.4, the initial fluid model is tuned against the experimental data from DL, CCE and separator tests until a good match was obtained.



Figure 3.4 Flow chart for fluid model development

Figure 3.5 shows the errors of the measured values from the laboratory tests and tuned values from the fluid model. These values include relative oil volume (ROV), gas/oil ratio (GOR), and oil density and viscosity. Due to confidential information, the errors between these values are used instead of actual values. It is seen that the errors for ROV, oil density and viscosity are small. Although the errors for GOR is relatively large in the pressure range of 0 - 10,000 kPa, they follow the changing trend and match well in the pressure range of 10,000 - 40,000 kPa. Table 3.1 presents the error between experimental and fluid model results at saturation pressure for GOR, and formation volume factor (FVF). Overall, a good match is attained. The pressure-temperature (P-T) diagram of the fluid model is presented in in Figure 3.6.



Figure 3.5 Errors of measured experimental values with values from the fluid model



Table 3.1 Experimental and estimated fluid properties at saturation pressure

Figure 3.6 Pressure-temperature (P-T) diagram of the fluid model

3.3.2 Reservoir Modeling

Figure 3.7 shows the workflow of reservoir modeling. First, a 3-dimensional reservoir block model is built with properties listed in Table 3.2. The dimensions of the block model are 1219 m x 321 m x 6 m. The five-layer block model, shown in Figure 3.8, consists of one injector and one producer, with a distance of 1146 m between them. The grid block size is determined after running multiple cases with various grid block sizes in the reservoir model, from which the optimum is chosen as the one meets the simulation accuracy and acceptable run time.



Figure 3.7 Reservoir modeling workflow

Parameter	Value			
Grid block system	50 x 32 x 5			
Grid block sizes	$\Delta x = 24.38 \text{ m}, \ \Delta y = 9.75 \text{ m}$			
	$\Delta z = 1.52 \text{ m}, 0.91 \text{ m}, 1.52 \text{ m}, 1.22 \text{ m}, 0.91 \text{ m}$			
Block size	1219 m x 312 m x 6 m			
Porosity	1600*0.15, 1600*0.1, 1600*0.2, 1600*0.06,			
	1600*0.13			
Horizontal permeability (mD)	1600*10, 1600*5, 1600*15, 1600*5, 1600*15			
Vertical permeability (mD)	Equals to horizontal permeability*0.1			
Initial water saturation	0.03			
Initial reservoir pressure	42,446 kPa			
Initial reservoir temperature	100°C			
Temperature near injector well	20°C and 100°C			

Table 3.2 Prop	perties of the	block model
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Figure 3.8 3-dimensional model for LSWI

After imputing the reservoir properties, the well-tuned EOS fluid model (described in section 3.3.1) is imported. Two sets of relative permeability curves (Figure 3.9) representing high and low salinity water are defined and used for interpolation to model wettability alteration by LSWI. The relative permeability curves for high salinity water represent a more oil-wet condition, and those for low salinity water represent a more water-wet condition.



Figure 3.9 Relative permeability for high and low salinity water

Subsequently, the LSWI process wizard is defined with input pertaining to formation water and injection water composition and interpolation approach. The composition of formation water initially present in the reservoir is listed in Table 3.3, which is used as input for the block model. According to the log-inject-log test results from McGuire et al. [20], an upper salinity threshold of approximately 5000 ppm is acknowledged to result in improved oil recovery by LSWI. Therefore, 5000 ppm is chosen as the salinity for the LSWI in this study. The average content of calcite cement is chosen to be 2% and dolomite is 0, according to the sedimentology study on the reservoir which is representative of clean sandstone [61]. Dissolution and precipitation of calcite and dolomite near the injection well is investigated.

Component	Formation Water		Low Salinity Water	
	ppm	Molality (mol/kg)	ррт	Molality (mol/kg)
Na ⁺ , mg/L	35,671	1.55	1,535	0.067
Mg^{2+} , mg/L	330	0.014	183	0.0076
Ca ²⁺ , mg/L	3,599	0.090	59	0.0015
K ⁺ , mg/L	225	0.0058	57	0.0015
Cl ⁻ , mg/L	62,371	1.76	2,761	0.078
SO4 ²⁻ , mg/L	233	0.0024	387	0.0040
HCO ₃ -, mg/L	-	-	18	0.00030
Total	102,430	-	5,000	-

Table 3.3 Composition of formation and injection water

Three approaches to relative permeability interpolation are used in the LSWI process wizard: (1) simple interpolation in terms of aqueous component Na⁺ concentration; (2) ion exchange interpolation in terms of Na - X equivalent fraction; and (3) mineral volume fraction interpolation in terms of porosity changes due to mineral dissolution. By using these three different interpolants, interpolations are carried out between the two defined relative permeability curves (Figure 3.9) as described in section 3.2.2 with the input upper and low bound of interpolant values shown in Table 3.4. Moreover, to investigate the effect of injection temperature, two scenarios were evaluated: 20°C and 100°C near the injection well.

Interpolation Approach	Na ⁺ concentration	Na-X fraction	Mineral volume fraction
Interpolant Value 1	35,000 ppm	0.42	0
Interpolant Value 2	5,000 ppm	0.15	-0.002

Table 3.4 Input interpolant value for different interpolation approaches

3.4 Results and Discussion

In this section, the effect of temperature and different approaches to relative permeability interpolation are evaluated in terms of oil recovery, mineral dissolution/precipitation, and changes in pH. Calcite dissolution and dolomite precipitation, and pH changes are examined with respect to time of injection and distance from the near-well region.

3.4.1 Oil Recovery

The effect of interpolation approaches to relative permeability and temperature near injector on oil recovery factor is shown in Figure 3.10. The ultimate oil recoveries of all scenarios are reported by the end of injection (year 2030). The oil recovery factor from the three interpolation approaches conducted at 20°C is approximately 6-9% less compared to those conducted at 100°C. The lower temperature tends to reduce the effectiveness of LSWI since lower oil recovery factors are observed at 20°C irrespective of the interpolation approach (Figure 3.10).





Figure 3.10 Oil recovery factor of three interpolation approaches at injection temperature of 20°C and 100°C

The effectiveness of LSWI is modeled with multi-component ion exchange (MIE) effect and a shift in relative permeability curves. As shown in Eq. (17), which is used to calculate reaction rate in the simulation, reduction in temperature leads to decreased reaction rate, which hinders the MIE effect on the negatively charged surfaces. Moreover, both the chemical equilibrium constant and selectivity coefficient are temperature dependent. If the forward reaction is exothermic, increasing temperature decreases the equilibrium constant. However, if the forward reaction is endothermic, increasing temperature increases the equilibrium constant. According to Le Chatelier's Principle, a dynamic equilibrium is disturbed by changes of condition (i.e., temperature). As the condition changes, the position of equilibrium shifts to counteract the change and re-establish equilibrium. The chemical reactions and ionic exchange reactions considered in section 3.2.1 are endothermic in the forward direction. Thus, with a decrease in temperature, the position of equilibrium tends to move in such a way to increase temperature, resulting in more in-situ $Ca - X_2$, and $Mg - X_2$ and less H^+ compared to the temperature of 100°C, which contributes to the reduction in oil recovery.

Furthermore, the effect of interpolation approach on oil recovery at 20°C and 100°C is compared. The differences in oil recovery are with 2% and 3% for injection temperature of 20°C and 100°C, respectively. It is seen that irrespective of the injection temperature, the effect of interpolation techniques to relative permeability curves has minor effect on oil recovery. Temperature has more significant impact on oil recovery compared to the interpolation techniques used.

3.4.2 Changes in pH

The effect of LSWI on pH was studied with respect to time and distance. Figure 3.11 shows the pH changes across layer 2 from the injector to the producer in the block model in year 2021, 2024, 2027, and 2030. Initially, in year 2021, the reservoir model is in equilibrium with formation water, showing a pH value of 5.5. As LSW is injected, a significant pH difference is

observed between the two near-injection well cases. Using 20°C as the injection temperature results in a pH value of approximately 8.8 compared to 7.3 for injection at 100°C. Between the injector and initial formation water, there exists a transition zone where pH of both cases decreases. However, pH at 20°C decreases to lower level than that at 100°C after some distance.



Figure 3.11 pH changes of linear path layer 2 at 20°C and 100°C

Figure 3.12 shows the temperature and pH profile determined using the simple interpolation approach. This was used to determine whether the changes in pH are a temperature effect. When injecting low salinity water at 20°C, a transition zone of temperature from 20°C to 100°C is observed, similar to Figure 3.11. It is observed that pH is higher near the injection well at 20°C and decreases along the prevailing direction of the injection fluid. The pH values drop to lower than those of 100°C after the temperature is increased to near 65°C (Figure 3.12). These observations in pH could be mainly caused by the temperature. Due to the presence of bicarbonate ions (HCO_3^-) in the injection water, the effect of temperature is notable. The reaction shown in Eq. (18) is endothermic. As low salinity water at 20°C encounters formation water of 100°C, Eq. (18) tends to move to the right to compensate for the temperature difference and re-establish equilibrium, resulting in pH decrease at higher temperature.

 $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$



Figure 3.12 Temperature and pH profile using simple interpolation approach Additionally, the relationships between pH and concentrations of bicarbonate ions (HCO_3^-) are investigated with Figure 3.13, showing pH and HCO_3^- concentration at the end of injection (year 2030) across a linear path of layer 2 in the block model. It is observed that the changing trend for cases using ion exchange interpolation differs significantly from the ones using simple interpolation and mineral fraction interpolation. For the cases using simple and mineral volume fraction interpolation with injection temperature of 20°C (Figure 3.13(a)), from 0 to approximately 110 m away from the injector, pH changes display the opposite trend of $HCO_3^$ concentration, which decreases with increasing HCO_3^- concentration. However, from 110m to near the producer, pH changes with the trend of HCO_3^- concentration. With injection temperature of 100°C (Figure 3.13(b)), pH changes show continuously the opposite changing trend of HCO_3^- concentration from the injector to the producer. We suppose this difference in pH changing trend with HCO_3^- concentration is mainly due to temperature. When the temperature of the injected low salinity water is the same as reservoir temperature (100°C), pH decreases with increasing HCO_3^- concentration. However, when the temperature of the injected low salinity water is significantly lower (20°C) than the reservoir temperature (100°C),

due to the existence of temperature transition zone while mixing the 20°C injected water with 100° C formation water, different changing trend of pH with HCO_3^- concentration is observed.



Figure 3.13 Relationship between pH and bicarbonate concentration after LSWI at (a) 20°C and (b) 100°C at the end of LSWI (year 2030)

Figure 3.14 shows the temperature profile after LSWI (year 2030). When injecting low salinity water with temperature of 20°C, it mixes with the water in the reservoir at 100°C, forming a temperature transition zone (0 – 300 m). From 0 to 110 m in Figure 3.13 (a), i.e., from 20°C to 65°C (mineral volume fraction interpolation) or 71°C (simple and ion exchange interpolation) in Figure 3.14, pH decreases with HCO_3^- concentration. However, after reaching 65°C or 71°C in the transition zone, further increase in temperature leads equation (13) to move to the left, resulting in higher concentration of HCO_3^- and higher pH. In this case, HCO_3^- acts like a buffer for pH changes with the effect of temperature.



Figure 3.14 Temperature profile for scenarios with injection temperature of 20°C after LSWI For the cases using ion exchange interpolation in Figure 3.13, showing relationship between pH and HCO_3^- concentration different from the cases using simple and mineral volume fraction interpolation, indicating other influencing factors besides temperature. It is seen from Figure 3.13 that the concentration of HCO_3^- is the highest at the distance of around 350 m for injection temperature 20°C (Figure 3.13 (a)) and 540 m for injection temperature 100°C (Figure 3.13 (b)), which is about 0.020 - 0.025 higher than the other two interpolation approaches in molality. This evident difference might be caused by the reduction of Ca²⁺ concentration. The concentration profile of Ca^{2+} shown in Figure 3.15 indicates that Ca^{2+} concentration is the lowest at around 300 - 400 m (20°C) and 500 - 560 m (100°C). This reduction in Ca²⁺ concentration results in Eq. (19) to move to the left direction, which could further lead Eq. (18) to move to the left direction. Thus, HCO_3^- concentration increases. To explain the reduction in Ca²⁺ along the flow path, the MIE during the flow transportation might be responsible. As low salinity water is injected and transported along the flow path, some Ca²⁺ might reabsorb onto the clay mineral surface along the fluid transportation, which gives rise to the decrease in Ca²⁺ concentration.

$$CO_3^{2-} + Ca^{2+} \rightleftharpoons CaCO_3 \tag{19}$$



Figure 3.15 Ca²⁺ molality profile at the end of LSWI with injection temperature of 20°C and 100° C

The aerial view of the pH profile at the end of injection (year 2030) is shown in Figure 3.16 (20°C) and Figure 3.17 (100°C). As shown from the figures, the difference in final pH between scenarios using simple interpolation and mineral volume fraction interpolation are not significant. Results from the ion exchange interpolation approach indicate a broader range of pH increase, but the oil recovery is the lowest irrespective of the temperature (as observed in Figure 3.10). From this finding, one can infer that increase in pH cannot be used as an evaluation for LSE. An increase in pH does not guarantee improved oil recovery by LSWI, even though increased pH was proposed by McGuire et al. [20] as a potential LSWI mechanism. This agrees with the observation reported by Zhang et al.[62]. They conducted secondary and tertiary core flooding experiments to investigate LSWI. Both slight increase and decrease in pH of the effluent were observed after LSWI, showing no clear relationship between pH of the effluent and oil recovery.

20°C near Injector Well



Figure 3.16 Aerial view of pH profile after LSWI at 20°C in year 2030



Figure 3.17 Aerial view of pH changes after LSWI at 100°C in year 2030

3.4.3 Mineral Dissolution and Precipitation

Dissolution and precipitation of calcite and dolomite due to LSWI were investigated. In CMG-GEM, positive values indicate precipitation and negative values indicate dissolution. Since the mineral dissolution and precipitation are only observed near the injector, Figure 3.18 and Figure 3.19 are plotted from 0 to 60/80 m away from the injector. Results indicate that dissolution of calcite and precipitation of dolomite are more significant with injection



temperature of 100°C compared to 20°C. It is also observed that dissolution of calcite increases with time and the increasing rate is faster with injection temperature of 100°C.

Figure 3.18 Calcite dissolution in layer 2



Figure 3.19 Dolomite precipitation in layer 2

Initially in the reservoir block model, calcite is in equilibrium with formation water with pH value of 5.5, which is a slightly acidic environment. However, with the injection of low salinity, pH is increased to above 7 near the injector. According to Sjöberg [63], no pH effect on calcite dissolution was found in the pH range of 7.5 to 8.5. With this pH range, concentration of

calcium begins to play a role. Calcite dissolution/precipitation is generally described with Eq. (20) in a basic environment. With the injection of LSW, a drastic decrease in Ca^{2+} compared to the formation water takes place near the injector well. This decrease in Ca^{2+} concentration leads Eq. (20) moving in the right direction, promoting the dissolution of calcite minerals. Due to the dissolution of calcite, a slight increase in Ca^{2+} and CO_3^{2-} concentration is expected. This continuous increase will lead Eq. (21) to move to the left, resulting dolomite precipitation. This is confirmed with the concentration changes of Ca^{2+} and Mg^{2+} in the early injection stage in Figure 3.20, which plotted the molality of Ca^{2+} and Mg^{2+} from January 2021 (start of injection) to August 2021. The molality of initial Mg^{2+} in formation water is 0.014 mol/kg, and the molality of Mg^{2+} injected low salinity water is 0.0076 mol/kg. It can be seen from Figure 3.20 that the molality of Mg^{2+} near the injector is around 0.002 – 0.006 for injection temperature of 20°C and 100°C, which is less than the Mg^{2+} molality in LSW, indicating the consumption of Mg^{2+} for dolomite precipitation.

$$Calcite \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{20}$$

$$Dolomite \rightleftharpoons Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$$
(21)



Figure 3.20 Molality changes in Ca²⁺ and Mg²⁺ at the beginning of injection for scenarios using simple interpolation approach

3.5 Conclusions

In this work, LSWI was modeled considering wettability alteration as the dominant mechanism and coupled with MIE effect. Three different approaches to relative permeability were used, which include simple interpolation in terms of aqueous component Na⁺, ion exchange interpolation in terms of equivalent fraction Na-X, and mineral volume fraction interpolation in terms of porosity changes due to mineral dissolution. Oil recovery, pH and temperature effect, and mineral dissolution/precipitation are investigated and compared. The following conclusions are drawn according to the results:

(1) There is an uncertainty in oil recovery resulting from the different approaches to relative permeability interpolation, as well as the temperature of the injection water in LSWI. When modeling LSWI, the choice of which approach to adopt and the consideration of temperature effect of the injection water are crucial since different interpolation approach for modeling wettability alteration and injection water temperature lead to differences in ultimate oil recovery.
- (2) Lowering the injection water temperature appears to reduce the effectiveness of LSWI. Temperature has an impact on the equilibrium constant of aqueous chemical reactions and the reaction rate of mineral dissolution/precipitation. At lower temperature, the reaction rate of ion exchange on the rock surface and mineral dissolution due to LSWI is lower, which reduces the low salinity effect.
- (3) The ion exchange interpolation approach results in the broadest range of pH increase and lowest oil recovery factor. Thus, pH value cannot be used as an evaluation for LSE; an increase in pH does not guarantee improved oil recovery by LSWI. There is no clear relationship between oil recovery factor and pH increase. Bicarbonate ions are found to have an influence on pH. At temperatures less than 65/71°C, pH decreases as bicarbonate concentration increases. At temperatures greater than 65/71°C, pH increases with bicarbonate concentration. With the effect of temperature, bicarbonate ions act as buffer for pH changes as LSW is injected into the reservoir block model.
- (4) Calcite dissolution and dolomite precipitation occur near the injection well. In a basic environment, calcium concentration plays an important role in the calcite dissolution process. However, pH is not effective in this condition. A drastic decrease in calcium ions in injecting low salinity water results in calcite dissolution near the injector well, which further promotes the precipitation of dolomite.

3.6 Appendix

The appendix shows some of the fundamental mathematical equations used in the simulator, CMG-GEMTM.

Flow Equations

The following are the material-balance and finite-difference equations for components in the oil and gas phases, as well as water components.

$$\psi_{i} \equiv \Delta T_{0}^{m} y_{io}^{m} (\Delta P^{n+1} - \gamma_{0}^{m} \Delta D) + \Delta T_{g}^{m} y_{ig}^{m} (\Delta P^{n+1} + \Delta P_{cog}^{m} - \gamma_{g}^{m} \Delta D) + q_{i}^{m}$$

$$- \frac{V}{\Delta t} [N_{i}^{n+1} - N_{i}^{n}] = 0 \quad i = 1, \dots, n_{c}$$

$$W$$
(3A-1)

$$\psi_{n_c+1} \equiv T_w^m (\Delta p^{n+1} - \Delta P_{cwo}^m - \gamma_w^m \Delta D) + q_{n_c+1}^m - \frac{V}{\Delta t} \left[N_{n_c+1}^{n+1} - N_{n_c+1}^n \right] = 0$$
(3A-2)

Where, N_i represent the moles of component i per unit of grid block volume, and N_{n_c+1} refers to the moles of water per unit of grid block volume, T_j is the transmissibility of phase j (o,w,and g), y_i is the mole fraction, P stands for pressure, P_c is capillary pressure, V refers to the grid block volume, γ_g is specific gravity or gravity term, Δt is timestep, and ψ is the function. Furthermore, N_i and N_{n_c+1} are related to phase molar densities (ρ), saturations (S), porosity (ϕ) and compositions (y_i) in the following equation.

$$N_i = \phi \left(\rho_o S_o y_{io} + \rho_g S_g y_{ig} \right) \quad i = 1, \dots, n_c$$
(3A-3)

$$N_{n_c+1} = \phi \rho_w S_w \tag{3A-4}$$

Phase-Equilibrium Equations

For a hydrocarbon system in a two-phase region at a given pressure, temperature, and N_i , the phase compositions and splits can be obtained by solving the thermodynamic-equilibrium equation (Eq. 3A-5) for the moles of component i in the gas phase (N_{ig}), which can be further used to calculate the moles of component i in the oil phase (N_{io}) from Eq. 3A-6.

$$g_i \equiv \ln f_{ig} - \ln f_{io} = 0 \tag{3A-5}$$

$$N_{io} = N_i - N_{ig}$$
 $i = 1, ..., n_c$ (3A-6)

Where, f_{ig} is fugacity of component i in gas phase and f_{io} is fugacity of component i in oil phase.

Saturation Equation

The saturations of water, oil, and gas $(S_w, S_o, and S_g)$ are related to N_i and phase molar densities $(\rho_w, \rho_o, and \rho_g)$.

$$S_w = N_{n_c+1}/(\phi\rho_w) \tag{3A-7}$$

$$S_o = (1 - S_w) \frac{N_o / \rho_o}{N_o / \rho_o + N_g / \rho_g}$$
(3A-8)

$$S_g = (1 - S_w) \frac{N_g / \rho_g}{N_o / \rho_o + N_g / \rho_g} = 1 - S_w - S_g$$
(3A-9)

Volume Consistency Equations

The equation is presented in Eq. (3A-10).

$$\psi'_{p} \equiv V \frac{\sum_{i=1}^{n_{c}+1} N_{i}^{n+1}}{(\rho_{o} S_{o} + \rho_{g} S_{g} + \rho_{w} S_{w})^{n+1}} - V \phi^{n+1} = 0$$
(3A-10)

The term of $V \frac{\sum_{i=1}^{n_c+1} N_i^{n+1}}{(\rho_o S_o + \rho_g S_g + \rho_w S_w)^{n+1}}$ represents the volume occupied by the fluids. The term of

 $V\phi^{n+1}$ refers to the pore volume. The volume of the fluids must equal to the pore volume.

Energy Balance Equation

The following energy balance equation is added to study the effect of temperature.

$$\begin{split} \psi_{T} &\equiv \Delta T_{o}^{m} H_{o}^{m} \left(\Delta p_{o}^{n+1} - \Delta \widetilde{\rho_{o}^{m}} g \Delta D \right) + \Delta T_{g}^{m} H_{g}^{m} \left(\Delta p_{o}^{n+1} + \Delta P_{cog}^{m} - \widetilde{\rho_{g}^{m}} g \Delta D \right) \\ &+ \Delta T_{w}^{m} H_{w}^{m} \left(\Delta p_{o}^{n+1} - \Delta P_{cwo}^{m} - \Delta \widetilde{\rho_{w}^{m}} g \Delta D \right) + \Delta \tau_{c}^{m} \Delta T^{n+1} \\ &+ Q_{loss} + \sum_{j} H_{j}^{n+1} q_{j}^{n+1} \\ &- \frac{V}{\Delta t} \left[\phi^{n+1} \left(\sum_{j} \rho_{j}^{n+1} S_{j}^{n+1} U_{j}^{n+1} \right) - \phi^{n} \left(\sum_{j} \rho_{j}^{n} S_{j}^{n} U_{j}^{n} \right) \right] \\ &- \frac{V}{\Delta t} \left[(1 - \phi_{0}) c_{R} \widetilde{\rho_{R}} (T^{n+1} - T^{n}) \right] = 0, \quad j = o, g, w \end{split}$$
(3A-10)

Where, c_R is the heat capacity of rock, H_j is molar enthalpy of phase j (oil, gas, and water), S_j is saturation of phase j, Q_{loss} is heat loss rate, T is temperature, U_j is the molar internal energy of phase j, $\tilde{\rho_R}$ is the rock mass density, and τ_c is the total thermal conductivity of the rock and fluids.

3.7 Nomenclature

Acronyms

API	American Petroleum Institute
BP	British Petroleum
CEC	Cation Exchange Capacity
Ca^{2+}	Calcium ion
CMG	Computer Modeling Group
CO_2	Carbon dioxide
CCE	Constant Composition Expansion
DL	Differential Liberation
EOR	Enhanced Oil Recovery
EOS	Equation of States
FVF	Formation Volume Factor
GOR	Gas Oil Ratio
LSWI	Low salinity water injection
Mg^{2+}	Magnesium ion
mD	Milli Darcy
MIE	Multi-component ion exchange
Na^+	Sodium ion
PHREEQC	pH-Redox-Equilibrium in C language
ROV	Relative Oil Volume
SO4 ²⁻	Sulfate ion
SRK	Soave-Redlich-Kwong
Temp	Temperature
WF	Weighting factor

Variables and parameters

par anicter s
Activity
Heat capacity of rock
Ionic strength
Activation energy
Fugacity of component i in gas phase
Fugacity of component i in oil phase
Molar enthalpy of phase j
Equilibrium constant
Molality
Moles of component i per unit of grid block volume
Moles of component i in phase j (j=g and o)
Pressure
Activity product
Reaction rate
Saturation
Temperature
Transmissibility in phase j (j=g, o, and w)
Molar internal energy of phase j
Compositions in phase j ($j=g$, o , and w)
Grid block volume

κ'	Selectivity coefficient
γ	Activity coefficient
$\gamma_{\rm g}$	Specific gravity
ζ	Equivalent fraction
ϕ	Porosity
τ	Total thermal conductivity

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Chapter 4 A Mechanistic Study of Wettability Alteration in Sandstone by Low Salinity Water Injection (LSWI) and CO₂ Low Salinity Water-Alternating-Gas (WAG) Injection

This chapter explores wettability changes during LSWI and CO2 LSWAG injection with a newly proposed displacement contact angle measurement. It is published in the conference of the Society of Core Analysis (SCA).

Abstract

Low salinity water injection (LSWI), an emerging Enhanced Oil Recovery (EOR) method, has proven to be effective in increasing oil recovery by wettability alteration. As low salinity water is injected into the reservoir, the pre-established equilibrium is disturbed. The chemical reactions among the oil/brine/rock system alters the existing wettability, resulting in enhanced oil recovery. Water-alternating-gas (WAG) injection is also a leading EOR flooding process in light to medium oil sandstone and carbonate reservoirs. A recently proposed hybrid EOR method, CO₂ low salinity (LS) WAG injection, shows promise based on experimental and simulation studies, compared to LSWI or CO2 injection alone. Wettability alteration is considered as the dominant mechanism for CO₂ LSWAG injection. In this study, a new displacement contact angle measurement which better mimics the actual displacement process taking place in a reservoir is used, aiming to investigate the effect of monovalent and divalent cations, CO₂, and injection schemes. It is found that the injection of NaCl low salinity water alters the wettability towards slightly water-wet, and the injection of CaCl₂ low salinity water alters the wettability towards slightly oil-wet. The injection of CO₂ promotes water-wetness and geochemical reactions between oil and brine. Injection scheme of CO₂ and NaCl low salinity water is more efficient than WAG cycle of CO₂/NaCl in wettability alteration towards more water-wet. However, the opposite trend is observed with CaCl₂ low salinity water, of which WAG cycle of CO₂/CaCl₂ is more efficient in altering wettability towards water-wet. The oil drop deformation process during LSWI resembles the process of oil removal using surfactant. As CO₂ is introduced, due to the acidic effect of CO₂ and ion exchange, it acts to wet the rock surface, leading to a more water-wet state. With introduction of CO₂, the oil drop deformation resembles the "roll-up" oil removal process.

4.1 Introduction

Low salinity water injection (LSWI) has been widely investigated and recognized as an effective enhanced oil recovery (EOR) method in both secondary and tertiary mode [1-3]. Compared to other chemical EOR methods, such as polymer or surfactant flooding, LSWI is advantageous due to its lower cost and reduced impact on the environment. Another advantage for LSWI is that it can be combined with other EOR methods to further improve oil recovery [4-6]. According to economic evaluations on chemical EOR methods by Al-Murayri et al. [7] and Muriel et al. [8], LSWI and CO₂ injection generate the highest net present value (NPV) and both methods are effective in increasing oil recovery. Therefore, a hybrid technique termed CO₂ low salinity water-alternating-gas (LSWAG) injection, which combines the EOR effect of both methods, has been developed over the last 15 years. CO₂ LSWAG injection has been studied through core flooding experiments, contact angle and interfacial tension (IFT) measurements, primarily with sandstone, at ambient or reservoir conditions. Most results confirm improved oil recovery using this hybrid technique, in both secondary and tertiary modes, with some exceptions [9-11]. Studies with negative or neutral outcomes are mainly due to the fact that the cores are strongly water-wet or contain very small amount of clay minerals. Clean water-wet sandstones may not be the most favourable reservoir conditions for CO₂ LSWAG injection [12, 13].

The proposed mechanisms of CO₂ LSWAG injection are a combination of LSWI and CO₂ WAG injection. Al-Abri et al. [14] proposed that the improved oil recovery by immiscible CO₂ LSWAG injection is due to mobility control and wettability alteration. The IFT between high salinity brine and oil reduces as CO₂ is introduced. However, changes in the IFT of low salinity brine and oil are not noticeable, indicating that IFT reduction is not a dominant mechanism in this process. They also suggest multi-component ionic exchange (MIE) in which Na⁺ substitutes the divalent cations (Mg²⁺) accounts for the higher oil recovery when injecting

monovalent NaCl brine compared to injection of MgCl₂ brine. Teklu et al. [15] claimed that CO₂ LSWAG injection improved oil recovery of conventional CO₂ WAG injection by forming in-situ carbonated water of higher CO₂ saturation in the brine phase due to the higher CO₂ solubility in low salinity water. This in-situ carbonated water promotes wettability alteration towards more water-wet and CO₂-brine IFT reduction, hence improved oil recovery. They also compared the CO₂-brine solubility model developed by Enick and Klara [16] and Li and Nghiem [17] with fresh water and 100,000 ppm NaCl at 71°C from 0 to 41 MPa. Both models show that CO₂ solubility in brine increases with pressure and CO₂ solubility is higher in fresh water. Chaturvedi et al. [18] and AlQuraishi et al. [11] suggest that fines migration and wettability alteration, mechanisms of LSWI, might be the dominant mechanisms for increased oil recovery by CO₂ LSWAG injection. The presence of clay minerals, especially kaolinite, is considered essential. However, this proposed mechanism is questioned by Zolfaghari et al. [19] as they achieved oil recovery in sandstone without kaolinite. Wettability alteration towards more water-wet was suggested by Al-Saedi et al. [20-22]. Based on the proposed mechanisms, wettability alteration and mobility control may be considered the dominant mechanisms in CO₂ LSWAG injection.

Wettability alteration taking place during CO₂ LSWAG injection could be ascribed to LSWI or the acidic effect of CO₂ [23, 24] or a combination of both. Drummond and Israelachvili [25] demonstrate wettability alteration indicated by contact angle measurements at ambient conditions for low salinity water varying from oil-wet to water-wet as pH is lower than 9 and from water-wet to intermediate-wet as pH is greater than 9. The pH during a LSWI is mostly below 9 [26], indicating the wettability alteration is more likely to be from water-wet to intermediate-wet [27]. The main functions of injecting CO₂ are oil swelling and viscosity reduction due to CO₂ solubility in oil, miscibility with oil if pressure is above minimum miscible pressure and wettability modification [21]. Since low salinity water and CO₂ both

impact wettability, the question remains as to whether the introduction of CO_2 in low salinity water will assist in promoting the geochemical reactions and low salinity effect. Generally, monovalent cations (Na⁺) and divalent cations (Ca²⁺ or Mg²⁺) have different impacts on the rock surface. The MIE mechanism by LSWI proposed by Lager et al. [28] demonstrates that multivalent cations, such as Ca²⁺, act as bridges between the oil polar components and the negatively charged rock surface, promoting oil-wetness. The mechanism of electrical double layer expansion by LSWI suggested by Ligthelm et al. [29] indicates that lowering the electrolyte content, especially reducing the content of multivalent cations, yields expansion of the electrical double layer surrounding the clay and oil, and an increase in zeta potential. This leads to wettability modification of the rock surface towards more water-wet. Wettability characterization is uncertain for CO₂ introduced with low salinity water in the sandstone/oil/brine/rock system since previous experimental data is limited.

To investigate wettability of the rock and fluid systems, direct or indirect and qualitative or quantitative methods can be used. Indirect and qualitative methods for characterizing rock wettability are capillarimetric method [30], spontaneous imbibition [31, 32], capillary pressure curves, and relative permeability method [33, 34]. Indirect and quantitative methods include the Amott and Amott-Harvey index method, USBM (U.S. Bureau of Mines) method, and the combined Amott/USBM method, which measure the average wettability of the rock samples, i.e., a macroscopic mean value of the rock wettability to a given fluid. Direct and quantitative method for characterizing the wettability of a specific surface is the contact angle measurement [35, 36], as well as the new SEM-MLA method introduced [37, 38]. Contact angle measurement works the best with pure fluids and well-prepared surfaces [39]. It can also be used to determine the effect of crude oil, brine chemistry, temperature and pressure on wettability. According to Arif et al. [40], direct contact angle measurements is a widely recognized technique for wettability characterization of rock/CO₂/brine or rock/oil/CO₂-

enriched-brine systems. In this research we used contact angle measurement as a method to evaluate wettability alteration. Our particular interest is understanding the ion exchange and chemical reactions of the rock/oil/brine/ and rock/oil/brine/CO₂ systems by comparing the effect of monovalent and divalent ions and the effect of CO₂ on water-wet and oil-wet sandstone under different injection sequences. Contact angle measurements may indeed be the best choice to differentiate any wettability changes as we are able to 1) conduct measurements with high temperature and pressure, under which the commonly used Amott or USBM method is not applicable [40, 41] and 2) still appreciate the core scale aspects of rock mineralogy and some differences in water-wet and oil-wet "real" surfaces [42].

The data for contact angle measurements on sandstone/crude oil/CO₂-enriched brine system is very limited. Jaeger et al. [43] performed captive bubble contact angle measurements with sandstone samples which were previously aged at room temperature with 1.5 wt% cyclohexanepentanoic acid in decane for two months. They reported a strongly water-wet condition, contact angle of 46°, of such system under 50°C and 20.7 MPa with 32,000 ppm synthetic seawater. Ameri et al. [44] conducted contact angle measurements on Bentheimer sandstones that are initially water-wet and oil-wet at elevated pressure from 0.2 to 14 MPa and with NaCl brine salinity ranging from 5000 to 35,000 ppm. They found that in initially waterwet sandstones, contact angle increases with pressure, and decreases with increasing NaCl brine concentration. The overall contact angle for using NaCl brine salinity ranging from 20,000 to 35,000 ppm is very low, less than 20°. The average contact angle for using 5000 ppm NaCl brine is 40° and the value when distilled water is used is 57°. This indicates that decreasing salinity of NaCl brine leads to a less water-wet state, which differs from the results obtained by Espinoza et al [45]. For initially oil-wet sandstone, samples were aged for 22 months with crude oil at 60°C. In the sub-critical and near-critial state region of CO₂ (0-9 MPa), contact angle increases is slightly higher with 35,000 ppm brine than with distilled water. However, the opposite is observed for super-critical state region of CO_2 (9-13 MPa), Seyyedi et al. [46] reported that contact angle values of the quartz with CO_2 -enriched brine are slightly higher than that with brine phase alone, indicating that injection of CO_2 alters wettability towards slightly less water-wet. However, Al-Abri et al. [14] reported contradictory results, showing that the contact angle was reduced with the addition of CO_2 , indicating a wettability alteration towards more water-wet. They conducted their contact angle measurements with Berea sandstone discs aged with crude oil at 60° for three weeks. They also found that changes in wettability are greater with divalent ions (Mg²⁺) than monovalent ions (Na⁺ and K⁺).

It is worth mentioning that there are limitations on these contact angle measurements that would result in misleading interpretations on the effect of CO₂ and low salinity water, and the working mechanisms of CO₂ LSWAG injection. In these measurements, the oil drop is introduced after the rock surface has been in contact with injection brine and CO₂, which is not representative of the actual displacement in a reservoir, where oil exists before the injection fluids. Therefore, in order to better capture and mimic the real displacement procedure taking place in a reservoir to investigate what triggers the wettability alteration during LSWI and CO₂ LSWAG injection, a displacement method developed by Sofla et al. [42] for measuring contact angle was employed in this study. We investigated the dynamic contact angle changes during the displacement process of LSWI, continuous CO2 and LSWI, and CO2 LSWAG injection, respectively. With this method, the interactions among crude oil, brine and CO₂ were investigated without the additional effect of capillary imbibition and drainage [47]. The objective is to compare the resulting wettability alteration (through contact angle measurements) due to multi-component ion exchange (MIE), chemical reactions, and injection sequence of low salinity water methods. This paper addresses the question as to whether or not the ionic charge and injection scheme play a role in differentiating LSWI and CO₂ LSWAG injection at the fluid-rock interaction level.

4.2 Material and Methods

Fluids. The oil phase used in this experiment is an offshore Newfoundland and Labrador (NL) light crude oil. Synthetic brines were prepared to mimic the Hibernia formation water and Grand Banks seawater. The two low salinity brines are 2000 mg/L NaCl and 2000 mg/L CaCl₂. Their chemical compositions and basic properties are presented in Table 4.1.

Component	FB	SW	NaCl	CaCl ₂
Na ⁺ , mg/L	35,671	10,974	786	/
Mg^{2+} , mg/L	330	1,310	/	/
Ca^{2+} , mg/L	3,599	420	/	721
K^+ , mg/L	255	407	/	/
Cl ⁻ , mg/L	62,371	19,740	1,214	1,279
SO_4^{2-} , mg/L	233	2,766	/	/
HCO_3 , mg/L	/	129	/	/
Total	102,430	35,746	2,000	2,000
pH@22°C	5.9	7.9	6.2	5.8
Density, g/cm ³	1.074	1.023	1.0	1.0
Oil Viscosity, cP	5.0			
Oil Density, g/cm ³	0.878			

Table 4.1 Compositions and properties of synthetic brines and oil

Legends: FB - formation brine; SW - seawater; / - not included

Rock sample. Berea sandstone with 80% quartz content and <2% clay content [37] was used in this study. The core samples with an approximate diameter of 2 cm were cut into 5-mm thin slices using MK-370EXP Tile Saw. The dust was blown off with pressurized nitrogen and the core slices were dried in oven overnight. The water-wet samples were immersed in formation brine for one day prior to conducting contact angle measurements. To obtain an oil-wet initial wettability, the core slices initially immersed in formation brine were removed to a beaker containing NL crude oil and aged at 98°C in the oven for six weeks as suggested by Sripal et al. [37] to obtain oil-wet conditions. Subsequently, the surface of the oil-wet samples was cleaned and immersed in formation water for one day before contact angle measurements.

Figure 4.1 illustrates the experimental setup used to perform contact angle measurements in this study. All experiments are conducted at ambient conditions. In order to mimic the actual

displacement taking place in a reservoir, the cell is initially filled with formation brine. Subsequently, an oil drop with radius ranging from 1.8 to 2.0 mm is introduced through the needle at the bottom of the cell and adheres onto the rock surface. The initial contact angles are measured after the system reached equilibrium, which is 1 hour after it is introduced into the system. This indicates the initial wettability of the rock surface and initial condition of an oil droplet in a reservoir.



Figure 4.1 Schematic diagram of contact angle measurement

A total of 13 experiments were completed, using the injection schemes outlined in Table 4.2. Each scenario was completed twice, once using NaCl as the LSW and again using CaCl₂ as the LSW.

Scenario	Injection Scheme				
#	Cycle 1 (60 mL)	Cycle 2 (20 mL)	Cycle 3 (20 mL)	Cycle 4 (20 mL)	
1	SW	SW	SW	SW	
2	SW	LSW	LSW	LSW	
3	LSW	LSW	LSW	LSW	
4	SW	CO ₂ (10ml)	LSW (25mL)	LSW (25mL)	
5	SW	CO ₂ /LSW	CO ₂ /LSW	CO ₂ /LSW	
6	LSW	CO ₂ (10mL)	LSW (25mL)	LSW (25mL)	
7	LSW	CO ₂ /LSW	CO ₂ /LSW	CO ₂ /LSW	

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Scenario 1 represents seawater injection. Scenario #2 and #3 represent LSWI. Scenarios #4 and #6 represents seawater or low salinity water injection, followed by continuous CO₂ injection and LSWI. Scenario #5 and #7 represent seawater or low salinity water injection, followed by LSWAG injection. Brines and CO₂ were injected through the injection inlet into the cell to displace the existing fluid. The injection speed was controlled so that the oil drop remains attached on the rock surface throughout the experiment.

The total volume of the cell is 20 mL. In cycle 1, 60 mL of seawater or low salinity water is injected to ensure that the initial formation brine is fully displaced. The system is allowed to set for equilibrium for half an hour after every 20 mL of injection fluid and the reading at equilibrium state is taken. Figure 4.2, as an example, shows the contact angle changes during the half-an-hour equilibrium time of scenario #1, indicating that an equilibrium was gradually established.



Figure 4.2 Contact angle changes after seawater injection during half-an-hour equilibrium time (scenario #1)

After cycle 1, another 60 mL of CO_2 (g), low salinity water and a combination of both are further injected in cycles 2-4 representing the injection schemes of continuous CO_2 and low salinity water injection, and the CO_2 LSWAG process. Contact angles are measured dynamically for each injection cycle and measurements are taken half an hour after each injection cycle. Three distinct measurements are carried out to monitor repeatability. Contact angles are reported as averages of the three measurements. The change in contact angle is calculated using the equation below.

$$\Delta \theta \, [\%] = (\theta - \theta_{initial}) / \theta_{initial} \times 100 \tag{1}$$

where $\Delta\theta$ refers to the change in contact angle, θ is the value of contact angle measured after each injection cycle, and $\theta_{initial}$ is the initial contact angle measured with the presence of formation water. The reason for comparing changes instead of absolute contact angles is to avoid the influence of the samples and each scenario starts from the same point. Initial contact angle is also reported.

To calculate the uncertainty, or error propagation of $\Delta\theta$, the root-sum square method proposed by Kline and McClintock is used [48]. The effect of uncertainty $\sigma_{\Delta\theta}$ on the calculated $\Delta\theta$ can be expressed as follow:

$$\sigma_{\Delta\theta} = \sqrt{\sigma_{\theta}^2 * (\frac{\partial(\Delta\theta)}{\partial\theta})^2 + \sigma_{\theta_{initial}}^2 * (\frac{\partial(\Delta\theta)}{\partial\theta_{initial}})^2}$$
(2)

Subsequently, changes in contact angle with calculated uncertainty are plotted against injected volume to investigate the effect of low salinity water, injection of CO₂ and WAG injection schemes.

Moreover, in order to validate that the measured contact angle changes are mainly due to the chemical reactions (intermolecular forces) in the oil/brine/rock system, rather than gravitational force, we have estimated the Bond number (B_o) of the oil/seawater/brine system using equation from Li et al. [49].

$$B_o = \frac{\Delta \rho g L^2}{\gamma} \tag{3}$$

where $\Delta \rho$ is the density difference of oil and brine (kg/m³), *g* is gravitational acceleration (m/s²), *L* refers to the radius of curvature of oil drop (m), γ is surface tension (N/m). With the measured surface tension (31.5 mN/m), and oil drop radius in seawater (1.86 mm), Bond number is calculated to be 0.154, which is lower than 1, indicating that surface tension dominates.

4.3 Results and Discussion

As shown in Table 4.3, section 4.1 investigates the effect of seawater and low salinity water (scenario #1, #2 and #3) on wettability alteration of water-wet and oil-wet Berea sandstone samples. Section 4.2 discusses the effect of CO_2 by comparing scenario #2 and #4, and #3 and #6. Subsequently, the deformation process of the oil drops during the injection of low salinity water and CO_2 is investigated in section 4.3. In the end, section 4.4 studies the effect of different injection schemes by comparing CO_2 + LSW injection scheme to CO_2/LS WAG injection scheme (#4 and #5, and #6 and #7). The effect of monovalent and divalent cations is discussed and compared in all sections.

Section	Comp	arison of different scenarios
4.2.1	#1	SW + SW
4.5.1 Effect of Low Solinity Water	#2	SW + LSW (NaCl and CaCl ₂)
Effect of Low Samily water	#3	LSW + LSW (NaCl and CaCl ₂)
	#2	SW + LSW
4.3.2	#4	$SW + CO_2 + LSW$
Effect of CO ₂	#3	LSW + LSW
	#6	$LSW + CO_2 + LSW$
	#4	$SW + CO_2 + LSW$
4.3.4	#5	$SW + CO_2/LS WAG$
Effect of Injection Scheme	#6	$LSW + CO_2 + LSW$
	#7	LSW + CO ₂ /LS WAG

Table 4.3 Comparison of different scenarios

4.3.1 Effect of Low Salinity Water

Contact angle changes due to the injection of seawater alone, low salinity waters alone, and combinations of seawater and low salinity water are shown in Figure 4.3 and Figure 4.4 for

water-wet and oil-wet sandstones, respectively. These injection schemes mimic the displacement process of (1) seawater injection, (2) secondary seawater and tertiary LSWI, and (3) LSWI. Overall, changes in contact angle in the oil-wet samples are not as significant as in water-wet samples. However, it is worth comparing and understand the changing trend after each injection cycle, which could be an estimation for the potential changes in a core scale experiment.



Figure 4.3 Contact angle changes during seawater and low salinity water injection in waterwet sandstone (scenario #1, #2, #3)



Figure 4.4 Contact angle changes during seawater and low salinity water injection in oil-wet sandstone (scenario #1, #2, #3)

In Figure 4.3, the initial wettability of the rock sample is water-wet, with measured contact angles varying from 34° to 50° (average: $40.6^{\circ}\pm5.0^{\circ}$). Contact angle changes due to the injection of seawater are within 5%, which is not very significant. This indicates that the injection of seawater has negligible effect on the rock wettability. The trend of using NaCl and CaCl₂ in LSWI shows different impacts on wettability. The red arrow in Figure 4.3 indicates changing towards more oil-wet and the blue arrow suggests changing towards more water-wet. It is seen that NaCl alters the wettability towards more water-wet, around 10% less compared to initial contact angle, whereas CaCl₂ results in wettability alteration moving to less water-wet. A similar trend is also observed in the combined seawater and LSWI process. In Figure 4.4, the initial wettability of the rock sample is oil-wet, with measured contact angle varying from 117° to 155° (average: 133.0°±13.5°). For seawater injection (SW + SW), the contact angle remains almost constant throughout the process. The injection of NaCl LSW alters the rock wettability towards slightly less oil-wet (SW + NaCl, NaCl + NaCl) and use of CaCl₂ (SW + CaCl₂, CaCl₂

+ CaCl₂) alters the wettability towards more oil-wet. This observation agrees with that in the water-wet samples where NaCl promotes water-wetness and CaCl₂ promotes oil-wetness.

Generally, the configuration of water on rock mineral surfaces exist in two ways: (1) pendularring on contact points of grains; and (2) thin film on the mineral surfaces [50]. In this study, the oil drop is introduced after formation water and is kept attached to the surface throughout the experiment. Therefore, the model proposed is as shown in Figure 4.5, where a thin water film is formed between the rock and oil drop. A similar model was also proposed by Lee et al. [51]. They manufactured sand/clay like silica particles using simple anionic surface similar to sand grain and measured the thickness of this water film to be roughly 9-15 nm. According to their measurements on the simple wet system (fabricated simple anionic surface, similar to a sand grain) [51], the thickness of the water film on the silica/clay (sandstone-like) surface is thicker in brines with lower salinities (except for pure water). Therefore, in a system where the substrate is initially oil-wet, in order alter the wettability from oil-wet to intermediate-wet or water-wet, a thicker water film along the pore wall is needed.



Figure 4.5 A proposed model with water thin film forming between the rock/brine and oil/brine interface (Adapted from Lee et al. [51])

Based on the results from Figure 4.3 and Figure 4.4, it is observed that the use of monovalent cations as injection brine alters the wettability towards more water-wet, which agrees with the finding from Xie et al. [52] that monovalent cations (Na⁺) give rise to positive disjoining pressure; however, divalent cations (Ca²⁺) lead to negative disjoining pressure at the same

concentration. Negative disjoining pressure between rock surface and oil droplet when CaCl was used as injection brines indicates the attractive force is dominant; thus, more oil-wet is expected for the rock surface. On the other hand, positive disjoining pressure suggests the repulsive force between the rock surface and oil droplet, leading to more water-wet.

4.3.2 Effect of CO₂

The wettability changes caused by CO₂ after seawater injection and LSWI (NaCl or CaCl₂) were investigated by comparing the contact angle changes in scenarios with CO₂ (#4 and #6) and without CO₂ (#2 and #3). Contact angle changes during cycle 2 – 4 are studied. For LSWI (#2 and #3), cycle 2-4 are injection of LSW. For CO₂ + LSW (#4 and #6), cycle 2 is injection of CO₂, cycle 3-4 are injection of LSW. To calculate the changes, $\theta_{initial}$ in Eq. (1) is not the initial value in cycle 1, but the equilibrium contact angle measured after cycle 1 ($\theta_{cycle 1,eq}$). Hence, Eq. (4) was used to calculate contact angle changes ($\Delta\theta$) and uncertainty was calculated according to Eq. (2).

$$\Delta\theta \, [\%] = \left(\theta - \theta_{cycle\ 1,eq}\right) / \theta_{cycle\ 1,eq} \times 100 \tag{4}$$

Based on this, all the scenarios investigated in this section will start from the same point in cycle 2 with respect to contact angle change.

Figure 4.6 and Figure 4.7 show the results of LSWI and $CO_2 + LSWI$ after seawater injection in water-wet and oil-wet samples respectively. When comparing scenario #2 (SW + LSW) and #4 (SW + CO₂ + LSW), the addition of CO₂ after seawater promotes water-wetness for both water-wet and oil-wet samples. After CO₂ injection, further injection of CaCl₂ changes the wettability towards more oil-wet, and the injection of NaCl changes further more towards water-wet.



Figure 4.6 Comparison of contact angle changes during LSWI and CO₂ + LSWI in water-wet sandstone after 1st cycle of seawater injection (scenario #2 and #4)



Figure 4.7 Comparison of contact angle changes during LSWI and CO₂ + LSWI in oil-wet sandstone after 1st cycle of seawater injection (scenario #2 and #4)

The contact angle changes of LSWI (scenario #3) and $CO_2 + LSWI$ (scenario #6) after LSWI in cycle 1 are shown in Figure 4.8 and Figure 4.9. Injection of LSW in cycle 2-4 has no significant impact on contact angle after the 1st cycle of LSWI. However, with the injection of CO_2 in cycle 2 and NaCl in cycle 3-4, CO_2 + NaCl alters wettability towards more water-wet

in both water-wet and oil-wet samples (Figure 4.8 and Figure 4.9). For scenario #6 (CO_2 + $CaCl_2$), CO_2 alters wettability towards more water-wet, whereas further injection of $CaCl_2$ changes the wettability to more oil-wet.



Figure 4.8 Comparison of contact angle changes during LSWI and CO₂ + LSWI in water-wet sandstone after 1st cycle of LSWI (scenario #3 and #6)



Figure 4.9 Comparison of contact angle changes during LSWI and CO₂ + LSWI in oil-wet sandstone after 1st cycle of LSWI (scenario #3 and #6)

It is also observed from Figure 4.8 and Figure 4.9 that CO_2 injected after $CaCl_2$ low salinity water alters wettability towards more water-wet compared to that injected after NaCl low salinity water. As suggested by Lager et al. [53], it is possible that some of the divalent cations are exchanged for monovalent cations during LSWI. Therefore, in our case, more Ca^{2+} on the rock surface is expected in scenario #6 with $CaCl_2$.

When CO_2 is in contact with water, it first dissolves according to reaction (5):

$$CO_2(g) \rightleftharpoons CO_2(aq) \tag{5}$$

At room temperature, solubility of $CO_2(g)$ is 0.034 mol/L. Subsequently, reaction (6) takes place to form H_2CO_3 . This reaction is kinetically slow and only a small fraction (0.2 – 1.0%) of dissolved CO₂, $CO_2(aq)$, is converted to H_2CO_3 .

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq) \tag{6}$$

However, this carbonic acid dissociates very rapidly at ambient conditions to bicarbonate [54], as shown in reaction (7). The bicarbonate electrolyte in the solution can also form CO_3^{2-} as shown by reaction (8).

$$H_2CO_3(aq) \rightleftharpoons HCO_3^- + H^+ \tag{7}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \tag{8}$$

With the injection of CO₂, some of the produced CO_3^{2-} would potentially react with the existing Ca²⁺ ions, forming CaCO₃, which results in equation (8) to move to the right direction, leading to slight increase in H⁺. Based on the selectivity of cation affinity to negatively charged surfaces from Velde [55], as shown below, the proton H⁺ has the strongest affinity to be adsorbed onto a negatively charged surface.

$$Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < H^+$$

Therefore, the generated H^+ is likely to replace the pre-attached divalent cations, resulting in more water-wetness. In this way, the injection of CO₂ after CaCl₂ low salinity water alters wettability towards more water-wet compared to injection of CO₂ after NaCl low salinity water.

4.3.3 Surfactant-Like Behavior of Oil Drop

During the injection of LSW and a combination of CO_2 and LSW in the water-wet and oil-wet samples, a surfactant-like deformation process of the oil drop is constantly observed when the initial equilibrium of the system is disturbed. The oil drop deformation with and without CO_2 is discussed respectively in the subsections.

4.3.3.1 Deformation in the Absence of CO₂

Figure 4.10 and Figure 4.11 illustrate the deformation process during the injection of NaCl LSW in water-wet and CaCl₂ LSW in oil-wet sandstones, respectively. For NaCl LSWI in water-wet sample, the contact angle varies from water-wet to intermediate-wet and then back to more water-wet while reaching equilibrium. For CaCl₂ LSWI in oil-wet sample, contact angle changes from oil-wet to intermediate-wet and then back to more oil-wet in the end.



Figure 4.10 Oil drop deformation process during NaCl LSWI in water-wet sandstone (scenario #3)



Figure 4.11 Oil drop deformation process in time during CaCl₂ LSWI in an oil-wet sandstone system (scenario #3)

Based on Figure 4.10 and Figure 4.11, the deformation process during LSWI resembles a surfactant-like behaviour. The potential removal of the droplet exhibits a "necking" or emulsification mechanism. One mechanism for LSWI proposed by McGuire et al. [56] suggests that the changes in wettability during low salinity water injection appear to be similar to the observations from alkaline and surfactant flooding. In this study, the interactions between the oil drop and injection fluids are more dominant due to the presence of just one oil drop. As listed inTable 4.1, the pH of the injection fluids is higher compared to that of the initial formation water. During the injection of low salinity water, in-situ "surfactants" are generated, as shown in Eq. (9), when the oil drop is in contact with the elevated pH fluid near the rock and oil surfaces. This improves oil recovery [56]. In this way, low salinity water injection is similar to micellar or surfactant flooding.

$$(R_1COO)_3R_2 + 3NaOH \leftrightarrow 3(R_1COONa) + R_2(OH)_3 \tag{9}$$

where R_1 and R_2 represent the R group, which consists of a group of carbon and hydrogen atoms.

According to the study of oil removal from soil surfaces by Miller and Raney [57], two approaches are proposed as mechanisms for oil removal from hydrophobic surfaces using surfactants: (1) roll-up resulting from wetting; and (2) emulsification resulting from reduction in interfacial tension (Figure 4.12).



Figure 4.12 Mechanisms of oil removal from surface by (1) roll-up and (2) emulsification (adapted from Miller and Raney [57])

4.3.3.2 Deformation with CO₂ Present

The top two pictures shown in Figure 4.13 are the oil drop deformation during injection of CO_2 + $CaCl_2$, (scenario #4) and the bottom two pictures are during $CaCl_2 LSWI$ (scenario #2). These two deformation processes resemble the two approaches in Figure 4.12. Without addition of CO_2 , the detachment of the oil drop is a saponification or emulsification process. However, the roll-up process is expected with CO_2 due to the geochemical reactions that change the wetting state of the contact point on the rock surface.



Figure 4.13 Comparison of oil drop deformation process: top (scenario #4): during CO₂ and CaCl₂ injection (roll-up); bottom (scenario #2): during CaCl₂ injection (emulsification) after seawater injection in water-wet sandstone

4.3.4 Effect of Injection Scheme

The impact of different injection schemes with respect to CO_2 is explored by comparing the scenarios of SW + CO_2 + LSW (#4) and SW + LSWAG (#5), and scenarios of LSW + CO_2 + LSW (#6) and LSW + LSWAG (#7). Contact angle changes of scenario #4 and #5 are shown in Figure 4.14 and Figure 4.15. It is observed that after 1st cycle of seawater injection, further injection of CO_2 + CaCl₂ alters wettability in the direction of more oil-wet, however, $CO_2/CaCl_2$ WAG injection alters rock wettability towards more water-wet. Injection schemes of CO_2 + NaCl and $CO_2/NaCl$ WAG both change the rock wettability to more water-wet, whereas changes are more significant for CO_2 + NaCl. The wettability changes by $CO_2/LSWAG$ processes (for both NaCl and CaCl₂) are not as significant as CO_2 + LSW injection when implemented after seawater injection (Figure 4.14 and Figure 4.15).



Figure 4.14 Comparison of contact angle changes during SW + CO₂ + LSWI and SW + CO₂/LS WAG injection in water-wet sandstone (scenario #4 and #5)



Figure 4.15 Comparison of contact angle changes during $SW + CO_2 + LSWI$ and $SW + CO_2/LSWAG$ injection in oil-wet sandstone (scenario #4 and #5), error bars are too small to be seen

Figure 4.16 and Figure 4.17 show the comparison between #6 (LSW + CO_2 + LSW) and #7 (LSW + CO_2 /LSWAG) in water-wet and oil-wet samples. The results in the figures show that the addition of CO_2 has a minor effect on the wettability for the CO_2 /NaCl WAG process. When

comparing $CO_2 + CaCl_2$ with $CO_2/CaCl_2$ WAG injection in both water-wet and oil-wet samples, the trend for wettability change is different. For the scheme of $CO_2 + CaCl_2$ injection, the addition of CO_2 promotes water-wetness of the rock, and the chasing $CaCl_2$ low salinity water changes the wettability back to more oil-wet. However, in the $CO_2/CaCl_2$ WAG process, the wettability is altered towards more water-wet.



Figure 4.16 Comparison of contact angle changes during LSWI, CO₂ and LSWI, and CO₂ LSWAG injection in water-wet sandstone (scenario #6 and #7), some error bars are too small to be seen



Figure 4.17 Comparison of contact angle changes during LSWI, CO₂ and LSWI, and CO₂ LSWAG injection in oil-wet sandstone (scenario #6 and #7), error bars are too small to be seen

The WAG process of CO₂ and CaCl₂ low salinity water leads to wettability alteration to slightly water-wet. With respect to the scenario of CO₂ + CaCl₂ (#6), even though CO₂ changes wettability to be more water-wet, the generated H⁺ is not sufficient. Thus, subsequent injection of CaCl₂ replaces the monovalent cations and alters the rock wettability towards more oil-wet. Summarising, if NaCl LSW is used, the continuous CO₂ + NaCl injection scheme is more efficient than WAG cycle of CO₂/NaCl in achieving a more water-wetness condition of sandstone. However, if CaCl₂ LSW is used, WAG cycle of CO₂/CaCl₂ can alter the rock wettability to more water-wet compared to continuous CO₂ + CaCl₂ injection.

4.4 Conclusions

In this study, a displacement method for measuring contact angle changes during the process of seawater injection, LSWI, CO_2 and LSWI, and CO_2 LSWAG injection has been conducted. Seawater, low salinity water with only monovalent and divalent cations were selected as the injection aqueous phases. The effect of these ions, oil drop deformation process, and the effect of CO_2 and injection scheme have been investigated.

- (1) It is found that for our Berea sandstone with an initial wettability of either water-wet and oil-wet, the injection of 2000 ppm NaCl water alters the wettability towards slightly water-wet, and the injection of 2000 ppm CaCl₂ alters the wettability towards slightly oil-wet. Low salinity water with divalent cation could increase the attraction forces between the oil/rock and oil/brine interfaces, promoting oil-wetness. However, low salinity with monovalent cation reduces the attraction forces, i.e., repulsive force increases, therefore, resulting in more water-wet.
- (2) The deformation process during LSWI resembles the process of oil removal using surfactant. This "surfactant-like" behaviour lowers the interfacial tension and contributes to increased oil recovery. As CO₂ is introduced, due to the acidic effect of CO₂, it acts to wet the rock surface, leading to a more water-wet state. Therefore, the oil removal or oil drop deformation resembles the "roll-up" oil removal process.
- (3) The injection of CO₂ promotes water-wetness and geochemical reactions between oil and brine. In the WAG process, more interactions between injection brine, CO₂ and pre-existing brine are expected, and this leads to different wettability alteration trend compared to CO₂ + LSWI. When NaCl LSW is used, continuous CO₂ + NaCl injection scheme is more efficient than WAG cycle of CO₂/NaCl in wettability alteration towards more water-wet. However, with CaCl₂ LSW, WAG cycle of CO₂/CaCl₂ can alter the rock wettability to more water-wet compared to continuous CO₂ + CaCl₂ injection.

4.5 Nomenclature

Acronyms

API	American Petroleum Institute
Bo	Bond number
Ca^{2+}	Calcium ion
CaCl ₂	Calcium chloride
Cl-	Chloride ion
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
EOR	Enhanced Oil Recovery
FB	Formation brine
---------------------------------	------------------------------------
g	Gravitational acceleration
HCO ₃ -	Bicarbonate ion
H_2CO_3	Carbonic acid
IFT	Interfacial tension
L	Radius of curvature of oil drop
LSW	Low salinity water
LSWAG	Low salinity water-alternating-gas
LSWI	Low salinity water injection
K^+	Potassium ion
KCl	Potassium chloride
Na ⁺	Sodium ion
NaCl	Sodium chloride
Na ₂ SO ₄	Sodium sulfate
NL	Newfoundland and Labrador
Mg^{2+}	Magnesium ion
MgCl ₂	Magnesium chloride
MIE	Multi-component ionic exchange
MLA	Mineral liberation analysis
SEM	Scanning electron microscope
SW	Seawater
USBM	U.S. Bureau of Mines

Greek letters

θ	Contact angle
ρ	Density
γ	Surface tension

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Chapter 5 Wettability and Novel Screening Methods for Low Salinity Water Injection in Sandstone

This chapter studies different contact angles obtained assuming different working mechanisms for LSWI. The possibility of linking the measured contact angle to relative permeability is explored. Novel screening methods for LSWI are proposed with the purpose to reduce the core flooding experimental runs. It is ready for submission

Abstract

Low salinity water injection (LSWI) is recognized as an effective enhanced oil recovery (EOR) technique in sandstone reservoirs. Numerous studies have investigated the underlying working mechanisms from the core- to reservoir-scale. In contrast, studies at the nano-scale, linking the observations from contact angle measurements to intermolecular forces and exploring the possibility to model wettability alteration through contact angles, are very limited. The objective of this study is to investigate disjoining pressure considering brines with different cation (Na⁺ and Ca²⁺) compositions and the relationship between disjoining pressure and measured contact angle. Geochemical modeling is performed to quantify the number of bridges between the oil and rock surface. The possibility of relating measured contact angle to relative permeability to model wettability alteration is explored and validated. It is found that Na⁺ cation leads to higher disjoining pressure and energy barrier for oil/brine and rock/brine interfaces to approach each other and promote water-wetness compared to Ca2+ cation. Moreover, the molality concentration of Ca^{2+} in the brine plays a more important role than the overall salinity in the ion exchange process and further affects wettability. Acceptable errors in oil recovery are reported when validating the wettability alteration model with core flooding experiments. Finally, in order to reduce the effort required to screen by core flooding experiments, two screening methods to obtain optimal salinity and composition for injection brine are proposed.

Keyword: Low salinity water injection (LSWI); intermolecular forces; contact angle measurement; relative permeability; wettability alteration model

5.1 Introduction

As the world demand for petroleum continues to increase and traditional oil recovery methods leave more than 50% of oil reserves not produced [1], various enhanced oil recovery (EOR) methods have been proposed to achieve higher oil production. Amongst these EOR methods, low salinity water injection (LSWI) has proven to be not only effective in both secondary and tertiary recovery mode [2], but also preserves more economic benefits and less environmental impact [3]. Mechanisms such as fines migration [4, 5], increased pH and interfacial tension (IFT) reduction [6, 7], osmotic pressure [8-12], salt-in effect [13], multi-component ionic exchange (MIE) [14, 15], expansion of electrical double layer [16-18], mineral dissolution [19], and wettability alteration [20-22] have been proposed in the past decades. Wettability alteration is the most commonly suggested mechanism and many of the other proposed mechanisms are related to it [2, 23]. However, most previous research was conducted on the core- to reservoir-scale. Studies performed at the nano-scale, linking the intermolecular forces to contact angle measurement, and linking contact angle measurement to relative permeability curves, are very limited.

Hirasaki [24] reviewed the physics and chemistry of wettability to provide guidance for investigating wettability mechanisms for petroleum reservoirs. Van der Waals and electrostatic forces originating from the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability [25-27] and non-DVLO surface forces (i.e., structural forces) should all be considered when describing contact angle through intermolecular surface forces [24]. Based on this, the extended DVLO theory, which includes structural force, has been used by several researchers [28-31] to investigate the impact of low salinity water on surface forces and wettability alteration. Xie et al. [31] studied the effect of salinity, cations, and clay minerals on disjoining pressure, and proposed a flowchart for screening low salinity water. Jalili and Tabrizy [29] related the disjoining pressure to contact angle through mathematical calculations and further

related the calculated contact angle to relative permeability curves for quartz/toluene and calcite/toluene systems. However, Liu et al. [28] pointed out the uncertainty in calculating disjoining pressure and contact angle. They conducted a simple sensitivity analysis on the Hamaker constant, empirical parameters for structural force, and retardation effect of van der Waals forces. They found that the difference in the calculated contact angle can be more than 10° [28]. The possible reasons for this difference might be due to use of unvalidated parameters for calculation, or the inherent limitation of excluding chemical reactions, such as multi-component ion exchange (MIE). However, this is not verified.

It has been widely reported that wettability alteration towards more water-wet leads to higher oil recovery in LSWI [20, 22, 28] and a shift in relative permeability [32-34]. Jerauld et al. [35] related relative permeability to salinity through a linear dependency without experimental verification. Tripathi and Mohanty [36] proposed three models of wettability alteration from oil-wet to intermediate-wet and from water-wet to intermediate-wet. In these models, oil saturation and relative permeability of water are salinity dependent. Shojaei et al. [37] tested their models with core flooding experiments and stated that oil relative permeability is salinity dependent in the LSWI process. However, results from some core flooding experiments showed that decreasing salinity might not always lead to an increase in oil recovery [22, 38]. The increase in oil recovery is somehow related to changes in wettability. Wettability alteration from intermediate-wet to water-wet was reported through contact angle changes and a shift in estimated relative permeability curves [37]. Since wettability alteration leads to changes in local contact angle and fluid distribution, which would further have an impact on relative permeability, is it possible to relate the measured contact angle to relative permeability curves to model wettability alteration due to LSWI? Jalili and Tabrizy [29] have proposed a model of wettability alteration (oil-wet to intermediate-wet) that relates calculated contact angle to relative permeability. Their model and the calculated contact angles are not verified; hence it is uncertain whether the method is representative of the suggested mechanisms for LSWI. It is inferred that assumptions of different working mechanisms for LSWI lead to different contact angles. The calculated contact angle is based on intermolecular forces, assuming that expansion of electric double layer (EDL) is the dominant mechanism. The measured contact angle is assumed to be dependent on EDL and MIE, however, this needs to be investigated and validated. Moreover, measured contact angle can be influenced by factors like the surface roughness and heterogeneity [39]. Since most surfaces are rough and heterogeneous to some extent, the only measurable value is the apparent contact angle [40]. Thus, apparent contact angle is measured and is referred to as contact angle throughout this paper.

Therefore, the objective of this study is to: (1) investigate wettability changes through nanoscale intermolecular forces, conventional and displacement contact angle measurements with high salinity water, seawater, and low salinity water with monovalent and divalent cations; (2) perform geochemical modeling that mimics the ion exchange and oil surface complexation of static conventional contact angle measurements to quantify the amount of oil surface species and electrostatic bridges; (3) investigate and compare the contact angles obtained from different assumptions of LSWI working mechanisms; (4) explore the possibility of relating contact angle to relative permeability with a wettability alteration model from intermediatewet to water-wet; and (5) use the proposed model in combination with disjoining pressure for brine salinity and composition screening.

5.2 Materials and Methods

Figure 5.1 shows the methodology flowchart. In the wettability study in step 1, we used the extended DLVO theory to calculate disjoining pressure and its corresponding contact angle (θ). This calculated value was compared to the experimental data measured using displacement and conventional methods. Contact angle calculated from disjoining pressure is representative of the assumption that expansion of electrical double layer (EDL) is dominant. The calculation is

based on intermolecular forces and ignoring chemical reactions like MIE. The conventional measuring method is based on the assumption of EDL and not fully-captured MIE. The displacement measuring method is based on the assumption of EDL and fully-captured MIE. We hypothesize that the displacement method can be used as a simplified method for LSWI screening which reduces the number of core flooding experimental runs. Geochemical modeling with respect to the contact point during static conventional contact angle measurement on Berea sandstone substrate was carried out to quantify the number of electrostatic bridges between oil and rock surface (> -COOCa) and available oil surface species $(-COOCa^+)$ for further potential ligand bonding. Subsequently, a method to generate relative permeability curves using the measured contact angle is proposed in step 2 assuming that the residual oil saturation decreases as wettability changes from intermediate-wet to waterwet. With the model and experimental data from Narsralla et al. [38], oil recovery from Berea sandstone core flooding experiments were compared with core-scale simulation in step 3 using the relative permeability curves generated in our study. Finally, based on the investigations on the contact angles obtained under different assumptions and the generated wettability model, screening procedures for an optimal brine salinity and composition are developed in step 4.



Figure 5.1 Methodology flowchart

5.2.1 Materials

Berea sandstone core slices approximately 2mm thick were used for contact angle measurement, and grinded powder was used for zeta potential measurement. The initial wettability of the Berea sandstone was water-wet. The oil phase was dead oil from offshore Newfoundland, with density of 0.878 g/cm³ and viscosity of 5 cp at standard condition. The total acid number (TAN) of this crude oil is zero [41]. The composition and properties of the synthetic formation brine, seawater, and low salinity water are also listed in Table 5.1.

Table 5.1	Composition	and properties	of brine
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Component	Formation Water	Seawater	NaCl	CaCl ₂
Na ⁺ , ppm	35,671	10,974	786	/
Mg ²⁺ , ppm	330	1,310	/	/
Ca ²⁺ , ppm	3,599	420	/	721
K ⁺ , ppm	255	407	/	/
Cl [–] , ppm	62,371	19,740	1,214	1,279
SO ₄ ²⁻ , ppm	233	2,766	/	/
HCO ₃ ⁻ , ppm	/	129	/	/
Total, ppm	102,430	35,746	2,000	2,000
Brine pH	5.5	7.9	6.2	5.8
Brine density, g/cm ³	1.08	1.02	1.00	1.00

/: not included

5.2.2 Experiment

Contact angle measurement. Contact angles were measured with the sessile drop method (Vinci IFT700) using conventional and displacement approaches. The measured contact angle is practically meaningful only in situation where the drop is axisymmetric in shape [42]. Another issue with nonideal surfaces is contact angle hysteresis when we have capillary imbibition and drainage, indicating that the measured apparent contact angle is within a range, instead of one value [43]. Thus, to decrease the effect of these factors, the core slices for contact angle measurement were handled as the procedure described in Ma et al. [44]. The differences in the measured left and right contact angle were kept within 2° for the conventional contact angle measurement. To monitor repeatability, three distinct measurements were carried out. Prior to each measurement, the core slices were immersed in formation water for 24 hours. For the conventional approach, the saturated core slice was placed into a measuring cell filled with brine. An oil drop was introduced and attached onto the rock surface. The contact angle at equilibrium was measured after 5 hours. A schematic diagram of the displacement approach is shown in Figure 5.2. In this approach, the measuring cell is initially filled with formation water, and an oil drop is introduced with the needle at the bottom of the cell. The equilibrium contact angle of the oil drop in formation water was measured after 1 hour. Subsequently, low salinity water or seawater was slowly injected into the measuring cell to displace the formation water until all the formation water initially present is fully displaced. An equilibrium contact angle was measured half an hour after the injection. The total injection and equilibrium time are 5

were conducted at ambient conditions.

hours, which is the same as the conventional approach equilibrium time. All measurements



Figure 5.2 Schematic diagram of displacement approach for measuring contact angle Figure 5.3, as an example, shows the contact angle changes during the half-an-hour equilibrium time of injecting seawater, indicating that an equilibrium was gradually established.



Figure 5.3 Contact angle changes after seawater injection during half-an-hour equilibrium Moreover, Figure 5.4 shows the changes in contact angle measured with displacement method during CaCl₂ low salinity water injection and additional 8 hours of equilibrium. It is seen that total equilibrium is established after 2 hours of injection and equilibrium. Thus, it is speculated that 5 hours of equilibrium is enough for measuring contact angle using conventional method.



Figure 5.4 Changes in contact angle during low salinity injection and equilibrium process *IFT measurement*. The pendant drop method was used to measure the interfacial tension (IFT) of the brine solution and oil with the Vinci IFT700 equipment at ambient condition. The measured IFT was used to calculate the contact angle from disjoining pressure isotherm.

Zeta potential measurement. Malvern Zetasizer Nano Series ZS instrument was used to measure the surface potential of the rock/brine and oil/brine interfaces. To measure the charge of rock/brine interface, 1 wt% powdered Berea sandstone was mixed with the brine using a magnetic stirrer for 1 hour. After the mixing, the solution was set for equilibrium for 24 hours. The method described by Sofla et al. [45] was employed to prepare the sample for oil/brine interface potential measurement. With this method, 1 vol% of oil is mixed with brine using a magnetic stirrer for 1 hour at elevated temperature to 60°C. Upon finishing, the sample was cooled down to room temperature and set to equilibrate for 1 hour. Prior to each zeta potential measurement, the disposable cell was carefully rinsed with ethanol and deionized water. To ensure repeatability, three measurements were performed, and the average was used for further calculation and analysis. All measurements were conducted at ambient conditions.

5.2.3 Extended DLVO Theory for Disjoining Pressure and Contact Angle Calculation

Based on the wettability review conducted by Hirasaki [24], disjoining pressure results from intermolecular forces between the rock/brine and oil/brine interfaces and consists of van der Waals, electrostatic, and structural forces, as shown in Eq. (1).

$$\Pi_{total}(h) = \Pi_{van}(h) + \Pi_{ele}(h) + \Pi_{str}(h)$$
(1)

where, *h* is the distance between the two interfaces, or the thickness of the water film, $\Pi_{total}(h)$ is the total disjoining pressure, $\Pi_{van}(h)$ is van der Waals force, $\Pi_{ele}(h)$ is electrostatic force, and $\Pi_{str}(h)$ is structural force. The disjoining pressure is the force that attracts or repulses the two interfaces. A positive disjoining pressure indicates repulsion of the two interfaces, which promotes water-wetness. A negative value corresponds to attraction and oil-wetness. The total disjoining pressure using extended DLVO theory is given as:

$$\Pi_{total}(h) = -\frac{A}{12\pi h^3} * \frac{15.96\frac{h}{\lambda} + 2}{(1 + 5.32\frac{h}{\lambda})^2} + nkT\left(\frac{2\varphi_1\varphi_2\cosh(\kappa h) - \varphi_1^2 - \varphi_2^2}{(\sinh(\kappa h))^2}\right) + A_0e^{-h/\lambda_0}$$
(2)

where, λ is London wavelength, n is the bulk ion concentration, φ_1 and φ_2 are the reduced potential, κ is the Debye length, k is Boltzmann constant, T is temperature, A_0 and λ_0 are force coefficient and decay length. Details regarding the disjoining pressure calculation can be found in Appendix 5.5.1.

The interaction potential ($\Delta\omega$) of the two interfaces separated by the water film can be calculated based on disjoining pressure described in Eq. (3) and equilibrium disjoining pressure Π_0 at equilibrium distance h_0 [24]:

$$\Delta \omega = \int_{h}^{h_0} [\Pi(h) - \Pi_0] dh$$
(3)

According to the contact angle prediction conducted by Churaev and Sobolev [46], contact angle can be related to disjoining pressure through Eq. (4):

$$\cos\theta = 1 + \frac{1}{\sigma_{ow,bulk}} \int_{h_0}^{\infty} \Pi_{totah}(h) dh$$
(4)

where, $\sigma_{ow,bulk}$ is the bulk oil/water interfacial tension and h_0 is the equilibrium film thickness where disjoining pressure is equal to the capillary pressure of the drop ($\Pi_0 = P_c$). However, as the contact angle is usually measured with the use of macroscopic drops, it is possible to accept that the equilibrium thickness of the water film corresponds to the condition under which the disjoining pressure is zero ($\Pi_0 = 0$). Thus, the equilibrium contact angle (θ_{eq}) can be approximated using Eq. (5):

$$\cos\theta_{eq} = 1 + \frac{1}{\sigma_{ow,bulk}} \left\{ -\frac{A}{12\pi{h_0}^2} * \frac{1}{1 + 5.32\frac{h_0}{\lambda}} + nkT \left[\frac{2\varphi_1\varphi_2}{\kappa\sinh(\kappa{h_0})} - (\varphi_1^2 + \varphi_2^2) \frac{\coth(\kappa{h_0}) - 1}{\kappa} \right] + A_0\lambda_0 e^{-h_0/\lambda_0} \right\}$$
(5)

With the assumption of $\Pi_0 = 0$, Eq. (4) can be expressed as Eq. (6):

$$\Delta \omega = \frac{A}{12\pi {h_0}^2} * \frac{1}{1+5.32\frac{h_0}{\lambda}} - \frac{A}{12\pi h^2} * \frac{1}{1+5.32\frac{h}{\lambda}} - nkT \left[\frac{2\varphi_1 \varphi_2}{\kappa \sinh(\kappa h_0)} - \frac{2\varphi_1 \varphi_2}{\kappa \sinh(\kappa h)}\right] + nkT \left[(\varphi_1^2 + \varphi_2^2) * \left(\frac{\coth(\kappa h_0)}{\kappa} - \frac{\coth(\kappa h)}{\kappa}\right)\right] - A_0 \lambda_0 * (e^{-h_0/\lambda_0} - e^{-h/\lambda_0})$$
(6)

5.2.4 Geochemical Modeling

To quantify the number of oil surface species and electrostatic bridges between oil/brine and rock/brine interfaces at equilibrium, geochemical modeling was performed using PHREEQC [47]. As the TBN is zero for the crude oil used in this study, the functional group at the oil surface is considered to be -COOH. The input parameters for the oil surface complexation model, rock surface ion exchange model, and solution reactions are shown in Table 5.2 [48, 49]. To estimate the number of exchangeable sites within the contact area of the oil drop and Berea sandstone core slice during the conventional contact angle measurement, the averaged cation exchange capacity (16 cmol/kg) and surface area (65 m²/g) from Farajzadeh et al. [50] was used, assuming that the mass contact between oil surface and rock surface is 0.01 g [50]. Thus, the exchangeable sites were estimated to be 1.6×10^{-6} mol.

Reaction	log K @25°C
Oil surface complexation	
$-COOH \rightleftharpoons -COO^- + H^+$	-5.0
$-COOH + Ca^{2+} \rightleftharpoons -COOCa^{+} + H^{+}$	-3.8
Rock surface ion exchange	
$> Na + -COOCa^+ \rightleftharpoons > -COOCa + Na^+$	1
$2 > Na + Ca^{2+} \rightleftharpoons > Ca + 2Na^+$	0.8
$> Na + H^+ \rightleftharpoons > H + Na^+$	4.6
Solution reaction	
$H_2 0 \rightleftharpoons H^+ + 0H^-$	-14
$CaOH^+ \rightleftharpoons Ca^{2+} + OH^-$	-1.22

Table 5.2 Model input parameters [48, 49]

5.2.5 Wettability Alteration Model

Clean sandstone tends to be water-wet, whereas many sandstone reservoirs are intermediatewet with contact angles ranging from 70° to 110° [51]. Based on previous work, wettability alteration can be achieved by LSWI [20, 21]. Nasralla et al. [22, 38] conducted Berea sandstone core flooding experiments considering LSWI as secondary recovery mode and contact angle measurements, indicating that the oil recovery increases with an increase in water-wetness, i.e., decrease in measured contact angle. Therefore, if oil recovery is assumed to increase with wettability changing towards more water-wet, residual oil saturation decreases with a reduction in contact angle or increase in $cos\theta$. Fjelde et al. [32] conducted core flooding experiments on sandstone with the injection of low salinity water. Changes in residual oil saturation during the injection process are shown in Figure 5.5. It is seen that the residual oil saturation decreases with injection pore volumes, which can also be expressed as a function of time with an exponential function.



Figure 5.5 Residual oil saturation and differential pressure across the composite core sample during LSWI [32]

Mahani et al. [52] visualized the contact angle changes with time of oil drops on glass substrate patched with clay particles in formation water and low salinity water. The changes in contact angle follows a trend and it is shown in Figure 5.6. Contact angles are seen to decrease with the injection of high salinity water and then further decrease with low salinity water. The red dashed line in Figure 5.6 represents the changing trend of contact angle with time, showing that the wettability changes from oil-wet to water-wet. Thus, it is be concluded that changes in contact angle can be a function of time, similar to the changes in residual oil saturation with time (Figure 5.5).



Figure 5.6 Oil detachment process and contact angle changes with time (adapted from Mahani et al. [52])

Therefore, we propose that oil recovery increases as the wettability varies from intermediatewet to water-wet due to LSWI. If the changes in wettability are expressed as variations in $cos\theta$, it is likely that we could assume an exponential relationship between the residual oil saturation and $cos\theta$, as shown in Figure 5.7.



Figure 5.7 The proposed relationship between residual oil saturation and $cos\theta$ Based on the proposed relationship of the residual oil saturation (S_{or}) and contact angle, the following equation is used to describe what Figure 5.7 shows.

$$S_{or} = a * e^{bcos\theta} \tag{7}$$

where, a and b are constants and can be obtained from boundary conditions. To set the boundary conditions for S_{or} , the following relationships are defined:

(1) Initial intermediate-wet condition ($\theta = 120^\circ$), initial oil saturation $S_{or,i}$ is

$$S_{or,i} = a * e^{-0.5b}$$
 (8)

(2) Final strongly water-wet condition ($\theta = 30^{\circ}$), the final oil saturation $S_{or,f}$ is:

$$S_{or,f} = a * e^{0.87b}$$
 (9)

With Eq. (8) and (9), the residual oil saturation in Eq (7) can be expressed as:

$$S_{or} = S_{or,i}^{0.64} S_{or,f}^{0.36} * \left(\frac{S_{or,f}}{S_{or,i}}\right)^{0.73cos\theta}$$
(10)

Relative permeability (k_r) is related to S_{or} through Corey correlation [53] assuming $k_{rw,max}$ and $k_{ro,max}$ equal to 1.

$$k_{rw} = \left(\frac{1 - S_w - S_{or}}{1 - S_{or} - S_{wi}}\right)^{(2+\lambda')/\lambda'} \tag{11}$$

$$k_{ro} = \left(\frac{S_w - S_{wi}}{1 - S_{or} - S_{wi}}\right)^{(2+3\lambda')/\lambda'}$$
(12)

where, λ' is the pore size distribution index. In this study, $\lambda' = 0.67$ is used as the pore size distribution index to represent Berea sandstone [54].

To assign appropriate limits for residual oil concentration, data from the literature was used. According to results from field single well chemical tracer tests in sandstone reservoirs conducted by McGuire et al. [7] and some core flooding experiments conducted on sandstone (Table 5.3), the final residual oil saturation after injecting formation water and low salinity water are 19 - 43% and 13 - 34%, respectively.

Table 5.3 Summaries of residual oil saturation after formation water and low salinity water injection from core flooding experiments and field single well chemical tracer tests

	Oil Pro	operties	Rock P	roperties	FW		LSW	
Ref	Density [g/cm ³]	Viscosity [cp]	Quartz [%]	Clay [%]	Salinity [ppm]	Sor	Salinity [ppm]	Sor
Field Single Well Chemical Tracer Tests								
[7]	/	/	/	/	22,000- 32,000	0.19-0.43	1,500- 2,200	0.13-0.34
	Core Flooding Experiments							
[55]	0.813	3.7 @20°C	96	4	97,575	0.35-0.43	/	/
[32]	/	1.5 @80°C	/	13	105,496	0.25	11-105	0.18-0.22
[56]	0.73	0.9 @25°C	80	5	24,951	0.31-0.40	250	0.21-0.30

Legend: Ref - reference; FW - formation water; LSW - low salinity water

Thus, the values for the lower limit of $S_{or,f}$ were set as 0.15 for formation water, and 0.1 for low salinity water. With Eq. (10), these ranges are covered as shown in Figure 5.8.



Figure 5.8 Relationship of residual oil saturation with contact angle

5.2.6 Validation of the Wettability Alteration Model

The experimental data from Nasralla et al. [38] was used for validation with CMG-STARS varying only the relative permeability curves generated using the model proposed in this work. CMG-STARS is a finite difference numerical simulator describing the mathematical equations such as Darcy's law, conservation equations, phase equilibrium equations, and etc. The governing equations for the multi-phase flow can be found in Appendix 5.5.2. Table 5.4 shows

the experimental results for contact angle (θ) measured with formation brine (FB), seawater (SW), aquifer low salinity water (AQ), and deionized water (DIW) [38].

Table 5.4 Experimental results of contact angle [56]						
Brine	FB	SW	AQ	DIW		
θ	60°	76°	49°	34°		

Table 5.4 Experimental results of contact angle [38]

Based on the core plug sizes used by Nasralla et al. [38], the grid block size in the core-scale simulation was chosen to be $15 \ cm \times 3.3 \ cm \times 3.3 \ cm$ with 30 blocks in the *x* direction. Figure 5.9 shows the schematic of the core-scale model for simulation. Properties such as porosity, permeability, initial water saturation (S_{wi}), and injected brine are shown in Table 5.5. Injection rate and production pressure were 0.5 cm³/min and 500 psi, respectively, which are the same as the parameter values from core flooding experiments [38]. The oil properties are listed in Table 5.6.



Figure 5.9 Schematic of the core-scale model

		I J		1 0
Core No.	Porosity [%]	Permeability [md]	S _{wi} [%]	Injected Brine
1	19.3	81.1	34.24	Formation water
2	18.6	66.7	32.25	Seawater
3	18.0	93.9	31.47	Low salinity water
4	18.6	77.6	33.37	Deionized water

Fable 5.5	Properties	and injected	l brine of	core plugs

Table 5.6 Oil Properties

Oil Densi	ty [g/cm ³]	Viscosi	ity [cp]
25°C	100°C	25°C	100°C
0.886	0.820	32.2	3.7

5.3 Results and Discussion

Zeta potentials of rock/brine and oil/brine interfaces were measured and used to calculate the disjoining pressure. Based on the calculated disjoining pressure, contact angles were calculated using Eq. (10) and compared to the measurements from the conventional and displacement methods. Subsequently, the proposed wettability alteration model, linking contact angle to relative permeability, were validated with core-scale simulations. A screening procedure for optimal brine salinity and composition is proposed.

5.3.1 Disjoining Pressure

Zeta potential measurements were conducted for 2000 ppm NaCl, CaCl₂, seawater and formation water with water-wet Berea sandstone powders and crude oil from offshore Newfoundland. The results are shown in Table 5.7. The objective of these measurements was to investigate the electrokinetic charge of the rock/brine and oil/brine interfaces under conditions where the salinity and compositions are different. Moreover, these measurements are used to calculate disjoining pressure and surface interaction potential.

Brine	Salinity	Rock/Brine	Oil/Brine	Debye length
	[ppm]	interface [eV]	interface [eV]	[1/nm]
NaCl	2,000	-49.0	-42.1	1.64
CaCl ₂	2,000	-15.7	-16.1	1.25
Seawater	35,746	-9.6	-13.0	0.37
Formation water	102,430	-4.8	-2.8	0.22

Table 5.7 Zeta potential measurements for rock/oil and oil/brine interfaces

The results in Table 5.7 show that the zeta potential of the negatively charges interfaces increases with decreasing salinity and 2000 ppm NaCl low salinity water (LSW) shows the strongest negatively charged interfaces. Since the oil carries negatively charged organic acids $(-COO^{-})$ and lowering the concentration of electrolyte leads to less positive charged cations being attached on the rock and oil surfaces, hence, the surface potential becomes more negative. According to Eq. (7), the thickness of the electric double layer (EDL) characterized by the Debye length $(1/\kappa)$ is sensitive to the ionic strength of the electrolyte (bulk concentration and

ion valence). Results in Table 5.7 show that low salinity water significantly increases the thickness of the electric double layer, which could potentially lead to a more water-wet condition. However, to better characterize the wettability alteration in an oil/brine/rock system in terms of intermolecular forces, the attractive van der Waal force and repulsive structural force should also be considered [24].

Figure 5.10 shows the calculated disjoining pressure of the water film, which separates the rock/brine and oil/brine interfaces. Positive disjoining pressure indicates repulsion between the two interfaces, and negative indicates attraction. For 2000 ppm NaCl and CaCl₂ LSW (Figure 5.10), as water film thickness decreases, disjoining pressure first increases to a peak positive value, which is the critical disjoining pressure ($\Pi_{critical}$), then decreases due to van der Waals attraction force, and finally increases sharply due to repulsive structural force. This type of disjoining pressure curve is categorized as metastable film, of which wettability can be altered by applying capillary pressure (P_c) higher than $\Pi_{critical}$ [57]. For seawater and formation water (Figure 5.10), disjoining pressure decreases to a trough due to van der Waals attraction force and increases sharply due to repulsive structural force within small separation. This type of disjoining pressure curve is categorized as unstable film, of which the rock surface prefers to be in contact with the oil phase, hence, wettability alteration occurs spontaneously [57]. It is implied that maintaining a more stable water film, by increasing disjoining pressure, could result in a more water-wet condition when only the intermolecular forces are considered, and chemical reactions are ignored.



Figure 5.10 Disjoining pressure of water film in oil/brine/Berea sandstone system Based on the disjoining pressure in Figure 5.10, the corresponding interaction potentials of the rock/brine and oil/brine interfaces are further calculated assuming that the equilibrium water film thickness is obtained at $P_c = 0$. The results are shown in Figure 5.11. Generally, a high disjoining pressure is likely to result in an energy barrier high enough to overcome. As seen from Figure 5.11, 2000 ppm NaCl LSW shows the highest energy barrier, indicating that it would be more difficult for the rock/brine and oil/brine interfaces to overcome the barrier to reach a thinner water film. However, there is almost no energy barrier for seawater and formation water. This suggest that the low disjoining pressure attracts the two interfaces and further destabilizes the water film. Once the film ruptures, the oil polar components tend to form direct bond with the rock surface and alters wettability towards more oil-wet. Therefore, if expansion of electric double layer (EDL) is the only mechanism considered for LSWI, lowering electrolyte concentration, or substituting divalent cations (Ca²⁺) with monovalent cations (Na⁺) promotes the stableness of the water film.



Figure 5.11 Interaction potential of oil/brine/Berea sandstone system

5.3.2 Contact Angle Comparison

The macroscopic contact angles were calculated with disjoining pressure at $P_c = 0$. This calculated value indicates the final equilibrium contact angle balanced by attractive van der Waals force and repulsive electric double layer force, ignoring chemical reactions like multicomponent ionic exchange (MIE). The measured contact angle was obtained using displacement and conventional methods. In the conventional method, no additional force is applied on the rock/brine and oil/brine interfaces, however, this force is considered in the displacement method. Both methods are capable of capturing the chemical reactions and effect of intermolecular forces. The results are shown in Table 5.8. The calculated and measured contact angle differ significantly, ranging from 11° to 29°. These differences could be due to the interplay of the repulsive electric double layer force and ion exchange taking place on the rock surface sites for contact angle measurements, whereas the calculated contact angle ignores the MIE effect.

Brine Calculated from Measured by	Contact Angle					
disjoining pressure displacement method convent	Measured by tional method					
2000 ppm NaCl 19° 31±1°	30±2°					
2000 ppm CaCl ₂ 15° $44\pm1^{\circ}$	35±1°					
Seawater / 35±2°	34±2°					

Table 5.8 Calculated and measured contact angle comparison at equilibrium

/: not calculated

According to Table 5.8, the difference between contact angle measured using displacement and conventional methods is negligible for 2000 ppm NaCl, whereas the difference is evident for 2000 ppm CaCl₂, which is around 9°. In order to explain the difference observed, the illustration in Figure 5.13 and number of electrostatic bridges (> -COOCa) and available oil surface species ($-COOCa^+$) for potential bridging obtained from geochemical modeling are employed.



Figure 5.12 Electrostatic bridge number of oil and negatively charged surfaces at equilibrium With the conventional method, the contact angle is affected by the number of electrostatic bridges > -COOCa of oil-rock binding and intermolecular surface forces. It can be seen from Figure 5.12 that the bridge number for 2000 ppm NaCl LSW is the lowest, almost zero. However, the highest bridge number is found when using 2000 ppm CaCl₂ LSW. A higher

bridge number indicates a more oil-wet condition. It is also observed from Figure 5.10 and Figure 5.11 that 2000 ppm CaCl₂ LSW shows a higher disjoining pressure and energy barrier than seawater and formation water. Thus, the difference in the measured contact angle using the conventional method between 2000 ppm CaCl₂ and seawater is negligible. However, for 2000 CaCl₂ and 2000 ppm NaCl, due to the higher disjoining pressure and lower bridge number, measured contact angle is lower with 2000 ppm NaCl.

With the displacement method, since the additional forces acting on the rock/brine and oil/brine interfaces are considered, a significant difference in measured contact angle is observed for 2000 ppm CaCl₂. Figure 5.13 illustrates the changes taking place on the interfaces whilst injecting LSW using the displacement method for measurement. Initially, the core slices are saturated with formation water, indicating that the water film formed between the rock and oil phase contains both divalent and monovalent cations (Ca²⁺ and Na⁺). As LSW is injected into the cell, the initial equilibrium is disturbed. With 2000 ppm NaCl LSW, Na⁺ tends to substitute Ca²⁺ which is exposed to the solution due to the equilibrium disturbance of the hydration shell. With 2000 ppm CaCl₂ LSW, the exposed Ca²⁺ tends to form bonds with the polar components of oil, promoting oil-wetness. Another reason for wettability changes (to slightly less waterwet compared to initial condition) during injection of 2000 ppm CaCl₂ is due to the injection process, which applies additional force on the rock/brine and oil/brine interfaces. This applied additional force acting on the interfaces makes overcoming the energy barrier for attraction of interfaces easier, and a less water-wet condition is expected compared to measurement with the conventional method.



Figure 5.13 Conceptual illustration of interactions during the injection of 2000 ppm NaCl LSW and 2000 ppm CaCl₂ LSW using displacement method

Figure 5.14 shows the interaction potential isotherms of NaCl and CaCl₂ for different capillary pressures. With the same capillary pressure applied, it can be seen that CaCl₂ LSW shows a significantly lower energy barrier for the two interfaces to attract than NaCl. Thus, with the injection of CaCl₂ LSW, the additional force acting to compress the interfaces contributes to overcoming the energy barrier and leads to faster rupture of the water film. This promotes the oil polar component to enter the ruptured water film and form a direct bond with the rock surface through Ca²⁺ acting as the bridge between the rock and oil phase. However, since the energy barrier when using 2000 ppm NaCl is harder to overcome, no significant difference is observed.



Figure 5.14 Interaction potential isotherms for (a) 2000 ppm NaCl and (b) 2000 ppm CaCl₂ for different capillary pressures

As shown in Figure 5.13, if additional force acting on the oil/brine and rock/brine interfaces is considered, the scenario with the higher amount of available $-COOCa^+$ species on the oil surface is likely to end up with a more oil-wet condition. This is due to higher attraction between the oil/brine and rock/brine interfaces and increasing bridging of Ca²⁺ with the negatively charged surfaces (> $-COO^-$). Table 5.9 shows the quantity of oil species on the surface at equilibrium and measured contact angle using the displacement method.

Surface species	Seawater	2000 ppm	2000 ppm
		CaCl ₂	NaCl
$-COO^{-}, \mu mol/m^{2}$	1.53	1.05	0.59
$-COOCa^+, \mu mol/m^2$	0.87	0.91	0.00
Contact angle	35±2°	44±1°	31±1°

Table 5.9 Oil surface species at equilibrium and contact angle (displacement method)

It is seen that the amount of $-COOCa^+$ species is the highest with formation water, offering the highest available $-COOCa^+$ species. When comparing the available $-COOCa^+$ species using seawater and 2000 ppm CaCl₂ LSW, use of 2000 ppm CaCl₂ LSW results in higher amount of oil surface species $-COOCa^+$ and highest contact angle, indicating that 2000 ppm CaCl₂ LSW promotes more oil-wetness compared to seawater. The molarity concentration of Ca²⁺ is 0.011 mol/L for seawater and 0.018 mol/L for 2000 ppm CaCl₂ LSW. This suggests that the concentration of Ca²⁺ cation might play a more important role than overall salinity in this scenario. Even though the overall salinity of 2000 ppm CaCl₂ is significantly lower than that of seawater (35,746 ppm), wettability alteration characterized by contact angle measurements varies significantly. Figure 5.15 further compares the contact angles and differences in surface species of $-COOCa^+$ and the number of electrostatic bridges formed through ligand bond (> -COOCa) under different Ca²⁺ molarities. It is seen that with higher Ca²⁺ molarity, the numbers of surface species ($-COOCa^+$) and bridges (> -COOCa) are higher. The values of the surface species and electrostatic bridges are obtained from modeling of equilibrium state, similar to the conventional method for measuring contact angle. With additional force acting on the oil/brine and rock/brine interface during displacement method which is more representative of the actual displacement process in a reservoir, the surface with higher number of $-COOCa^+$ is likely to bond with the rock surface once the oil/brine and rock/brine interface ruptures, promoting oil-wetness.



Figure 5.15 Surface species of -COOCa⁺ and number of bridges at different Ca²⁺ molarities and contact angles measured using displacing method

It can be concluded that the effect of LSWI is a combination of expansion of electric double layer and ion exchange on exchangeable sites. If no chemical reactions exist during the LSWI process, electric double layer repulsion is the dominant force that stabilizes the water film. Solutions containing a higher concentration of divalent cation tend to show a lower energy barrier for water film rupture and promote oil-wetness. Wettability characterization by contact angle measurement is capable of capturing the wettability changes of the rock surface on the specific site, which is in contact with oil. With the displacement method which resembles the actual displacement process taking place in a reservoir, additional pressure acts on the rock/brine and oil/brine interfaces, which could potentially accelerate the water film rupture process.

5.3.3 Contact Angle and Relative Permeability Curves

Based on the previous discussion, contact angle measurement can be used to characterize wettability of the rock surface, and hence can be used to predict the wettability changes if it is measured properly. Previous studies have related salinity, equivalent fraction of an aqueous component on exchanger to residual oil saturation and used as interpolants for relative permeability interpolation to model wettability alteration [32, 33, 58]. In this study, the possibility of relating contact angle measurements to relative permeability curves to model wettability alteration was explored.

The wettability alteration model developed in this study is based on the following assumptions:

- Wettability alteration from intermediate-wet to water-wet is the dominant mechanism for LSWI, characterized by a decrease in contact angle,
- (2) Residual oil saturation decreases as wettability is altered towards more water-wet and is linked to contact angle through an exponential function, and
- (3) The heterogeneity of the rock surface is not significant.

Based on these assumptions, a wettability alteration model dependent on contact angles was developed and relative permeability curves of injecting formation brine (FB), seawater (SW), aquifer low salinity water (AQ), and deionized water (DIW) were generated accordingly with the model using Eq. (10, 11, 12) and measured contact angle from Nasralla et al [37]. The generated relative permeability curves are shown in Figure 5.16, together with salinities of the

injection brines, the measured contact angle, and the oil recovery results obtained from core flooding experiments by Nasralla et al [37]. The red color in the figure indicates a more oil-wet condition, and the blue color indicates a more water-wet condition. From the figure, it can be seen that as the measured contact angle decreases from a high of 76° for SW to a low of 34° for DIW, the relative permeability curves shift from left to the right with the sequence of SW (76°), FB (60°), AQ (48°), and DIW (34°), indicating a wettability alteration towards more water-wet. This shift is accompanied by an increase in oil recovery from 62% to 86%.



Figure 5.16 Relative permeability curves generated using wettability alteration model and compared with oil recovery from core flooding experiments [38]

It is also observed that even though the salinity of seawater (54,680 ppm) is significantly lower than formation water (174,156 ppm), the measured contact angle is higher with seawater and oil recovery is lower. This could be due to the effect of electric double layer force with different brine compositions, or related chemical reactions, such as MIE effect etc. However, details to explain this difference is missing. The zeta potential measurements (Table 5.10) from Nasralla et al [37] only investigated the electrokinetic charge at the rock/brine and oil/brine interfaces with SW, AQ and DIW, showing that decrease in salinity leads to increase in negativity electrokinetic charges and wettability alteration towards more water-wet. The effect of formation water on electric double layer force is lacking. In this scenario, modeling wettability alteration induced by LSWI with only reduction in salinity might lead to unexpected errors and it is inferred that using measured contact angle to model wettability alteration could be more accurate than simply using salinity.

Zeta potential	FB	SW	AQ	DIW	
ζ _{rock/oil} [eV]	/	-5	-16	-21	
$\zeta_{\text{brine/oil}}[\text{eV}]$	/	-2	-16	-38	
/: not included					

Table 5.10 Zeta potential measurements from Nasralla et al [37]

The generated wettability alteration model was validated with core-scale simulation. In the core-scale simulation, core dimensions, rock and oil properties, injection rate, pressure and temperature are the same as those of the core flooding experiments. Oil recovery factor from core flooding experiments [38] and core-scale simulation, varying only the relative permeability curves generated through contact angle measurements, are compared and shown in Figure 5.17. The differences between oil recovery factor from the core flooding experiments and core-scale simulations are not significant, within 0-6%. This indicates that the proposed wettability alteration model has potential to model LSWI and predict oil recovery.



Figure 5.17 Oil recovery comparison between (a) core flooding experiments [38] and (b) core-scale simulation output

5.3.4 Screening Procedure

Previous discussions (section 5.3.1 – 5.3.3) suggest that the concentration of monovalent or divalent cations is more important than the overall salinity to determine the effectiveness of LSWI. Thus, simply using salinity as an interpolant and ignoring the effect of MIE and expansion of EDL to model wettability alteration could lead to significant errors in predicting low salinity effect. In addition, the conventional and displacement methods for measuring contact angle is capable of capturing the MIE and expansion of EDL due to LSWI. The validation of the wettability alteration model using measured contact angle is within acceptable errors in terms of oil recovery and indicates that it is possible to use this proposed model to predict the effectiveness of LSWI. Previous proposed wettability alteration modeling using overall salinity [35], salinity of an aqueous component [59], or equivalent fraction of an aqueous component on negatively charged rock surfaces [33] require core flooding experiments for history matching to obtain more accurate results. If core flooding experiments are chosen as a method to obtain an optimal brine salinity and composition, numerous
experiments will be conducted, which is very time-consuming, even though it would provide more accurate results of brine salinity and composition compared to modeling.

Hence, in order to reduce the number of experimental runs and, at the same time, provide more accurate predictions for optimal brine salinity and composition, we propose two screening methods for LSWI: (1) displacement contact angle measurement, or (2) generation of relative permeability curves using traditional contact angle measurement and calculation of disjoining pressure. Figure 5.18 shows the detailed steps for both methods. By applying the displacement contact angle method, contact angle is measured as described in section 5.2. The measuring chamber is initially filled with formation water before the introduction of an oil drop. After the oil drop is attached to the rock surface, brine is slowly injected into the chamber to displace the formation water. Contact angles measured at equilibrium are compared and the lowest value corresponds to the optimal brine salinity and composition. However, if this approach is not possible due to the constraints of the equipment, an alternative LSWI screening, method 2, which considers MIE, expansion of EDL, and wettability alteration can be employed. To model wettability alteration, first contact angle is measured, and relative permeability curves are generated accordingly with Eq. (10, 11, 12). To evaluate the water film stability formed between the oil/brine and rock/brine interfaces, disjoining pressure is calculated using Eq. (2). If relative permeability curves move towards more water-wet and higher disjoining pressure occur, an optimal salinity and composition of brine are achieved. However, if one of these requirements is not met, the screening process is restarted with another salinity or composition until both requirements are satisfied.



Figure 5.18 Screening procedure to obtain optimal brine salinity and composition

5.4 Conclusions

This work investigated the relationship between disjoining pressure and contact angle measurements. The possibility of relating contact angle to relative permeability to model wettability alteration was explored. Conclusions are presented as follows.

- (1) Disjoining pressure can be used to characterize the expansion of EDL due to LSWI; however, chemical reactions like MIE effect are not covered. When only the intermolecular force and expansion of EDL are considered (and chemical reactions like MIE are ignored) during LSWI, a more stable water film can be maintained by lowering the electrolyte concentration or substituting Ca²⁺ with Na⁺ cation. Low salinity water with monovalent cations leads to higher disjoining pressure and energy barrier between the oil/brine and rock/brine interfaces, resulting in a more water-wet condition.
- (2) When comparing a contact angle measured using the displacement method versus the static conventional method, there is no noticeable difference for 2000 ppm NaCl since the energy barrier is the highest. A significant difference (approximately 9°) is observed for 2000 ppm CaCl₂. This is due to the additional pressure acting on the rock/brine and

oil/brine interfaces, which could potentially accelerate the water film rupture process, leading to bridging of these interfaces through Ca²⁺.

- (3) The geochemical modeling showed that, compared with seawater, the 2000 ppm CaCl₂ LSW had a higher number of electrostatic bridges and oil surface species ($-COOCa^+$) available for further binding if the equilibrium is disturbed. This indicates that the molality concentration of Ca²⁺ cation in the injection brine plays a more important role than the overall salinity. Simply decreasing salinity might not lead to a more water-wet condition, however, decreasing the concentration of Ca²⁺ might contribute to altering the rock wettability towards more water-wet.
- (4) Measured contact angle can be used to model wettability alteration from intermediatewet to water-wet if the measurements are performed properly and the heterogeneity of the rock is not significant. The generated curves were used for core-scale simulation to model wettability alteration. Oil recovery factors obtained from the core-scale simulation were compared with core flooding experiments. The errors between the modeling and experiments are within an acceptable range (less than 6%).
- (5) In order to reduce the number of experimental runs required to obtain an optimal salinity and composition for injection brine, two screening methods are proposed: (1) displacement contact angle measurement; and (2) generation of relative permeability curves using traditional contact angle measurement and calculation of disjoining pressure.

5.5 Appendix

5.5.1 Calculations for van der Waals force, electrical force, and structural force

Van der Waals force is considered essential and important in all phenomena involving intermolecular forces [25]. The most commonly used approximate empirical expression for retarded van der Waals force is proposed by Gregory [60] and shown in Eq. (5A-1):

$$\Pi_{van}(h) = -\frac{A}{12\pi h^3} * \frac{15.96\frac{h}{\lambda} + 2}{(1 + 5.32\frac{h}{\lambda})^2}$$
(5A-1)

where, λ is London wavelength and is given as 100 nm [60] and A is Hamaker constant, which can be obtained through experiment or calculation [25]. In this study, we have adopted the Hamaker constant of 0.81×10^{-20} J from Xie et al. [31].

The charging of a surface in liquid could come from dissolution of protons from surface functional groups (i.e., carboxylic group, silanol group, and etc.), or the binding of ions from solution to previously uncharged surfaces or ion exchangeable surfaces. As the two charged surfaces approaching each other and the electric double layers overlap, the electrostatic forces arise. The approximation of the force between unequal diffuse double layer can be obtained assuming either constant charge or constant potential. With constant potential condition, it is assumed that there is always attraction between unequal diffuse layers even if they have the same sign. With constant charge condition, repulsion between the unequal layers is assumed. Eq. (5A-2) shows the expression for electrical double layer force with constant potential assumption and Eq. (5A-3) is the expression with constant charge assumption [61]:

$$\Pi_{edl}(h) = nkT\left(\frac{2\varphi_1\varphi_2\cosh(\kappa h) - \varphi_1^2 - \varphi_2^2}{(\sinh(\kappa h))^2}\right)$$
(5A-2)

$$\Pi_{edl}(h) = nkT\left(\frac{2\varphi_1\varphi_2\cosh(\kappa h) + \varphi_1^2 + \varphi_2^2}{(\sinh(\kappa h))^2}\right)$$
(5A-3)

where *n* is the bulk ion concentration, φ_1 and φ_2 are the reduced potential and can be calculated using Eq. (5A-4),and κ is the reciprocal Debye length, which can be calculated using Eq. (5A-5)

$$\varphi = \frac{ze\varphi_0}{kT} \tag{5A-4}$$

$$\kappa = \sqrt{\frac{e^2}{\varepsilon_0 \varepsilon_r k T} \sum_i c_i^0 Z_i^2}$$
(5A-5)

where z is the valence of a symmetrical electrolyte solution, e is the electron charge, φ_0 is surface potential, φ is reduced surface potential, k is Boltzmann constant, T is temperature, ε_0 is dielectric permittivity of vacuum, ε_r is relative permittivity of the electrolyte solution, c_i^0 is the bulk concentration of component i in particles per cubic meter, and Z_i is the valency of the *i*th ion.

Structural force, or solvation force, is a non-DLVO force, which acts in the ranges between the two interfaces in a medium when the DLVO forces (van der Waals and electrostatic forces) fail to describe the interaction [24, 25]. The structural force in a aqueous system can either be repulsive hydration force or attractive hydrophobic force [25]. In this study, we calculated the repulsive hydration force using Eq. (5A-6):

$$\Pi_{str}(h) = A_0 e^{-h/\lambda_0} \tag{5A-6}$$

where, A_0 and λ_0 are force coefficient and decay length. Despite the high uncertainty with these empirical parameters for calculating disjoining pressure [28], we have adopted the parameters used by Hirasaki [24]: $A_0 = 1.5 \times 10^{10}$ Pa and $\lambda_0 = 0.05$ nm for approximating a changing trend.

5.5.2 Governing equations in CMG-STARS modeling

This appendix mainly shows the summary of conservation equations. More details about other related equations like phase equilibrium equations and well equations can be found in the user's guide for CMG-STARS [62].

The conservation equation of flowing component i is presented as Eq. (5A-7):

$$\frac{\partial}{\partial t} \left[V_f \left(\rho_w S_w w_i + \rho_o S_o x_i + \rho_g S_g y_i \right) + V_v A d_i \right] \\
= \sum_{k=1}^{n_f} \left[T_w \rho_w w_i \Delta \Phi_w + T_o \rho_o x_i \Delta \Phi_o + T_g \rho_g y_i \Delta \Phi_g \right] + V \sum_{k=1}^{n_f} (s'_{ki} - s_{ki}) r_k \\
+ \sum_{k=i}^{n_f} \left[\phi D_{wi} \rho_w \Delta w_i + \phi D_{oi} \rho_o \Delta x_i + \phi D_{gi} \rho_g \Delta y_i \right] + \delta_{rw} \sum_{k=1}^{n_f} \rho_w q_a q_{wk} \\
+ \left[\rho_w q_{wk} w_i + \rho_o q_{ok} x_i + \rho_g q_{gk} y_i \right]$$
(5A-7)

where, $\frac{\partial}{\partial t} \left[V_f (\rho_w S_w w_i + \rho_o S_o x_i + \rho_g S_g y_i) + V_v A d_i \right]$ refers to the time-derivative of material accumulation. In this relation, V_f is the total fluid volume, V_v is the total void volume, w_i , x_i , and y_i represent the mole fraction of component i in the water, oil, and gas phase respectively, ρ_w , ρ_o , and ρ_g are densities of water, oil, and gas, and S_w , S_o , and S_g are saturations for water, oil and gas. The flow term for component i is represented with $[T_w \rho_w w_i \Delta \Phi_w + T_o \rho_o x_i \Delta \Phi_o + T_g \rho_g y_i \Delta \Phi_g + \phi D_{wi} \rho_w \Delta w_i + \phi D_{oi} \rho_o \Delta x_i + \phi D_{gi} \rho_g \Delta y_i]$. The well source term is expressed as $[\rho_w q_{wk} w_i + \rho_o q_{ok} x_i + \rho_g q_{gk} y_i]$ and the reaction source term is shown as $V \sum_{k=1}^{n_f} (s'_{ki} - s_{ki}) r_k$ for component i. $\sum_{k=1}^{n_f} \rho_w qaq_{wk}$ is aquifer source term for water component, where qaq_{wk} is the volumetric flow rate from block k to near aquifer. n_f is the number of neighboring regions or grid block faces.

The conservation equation of energy is shown as Eq. (5A-8):

$$\frac{\partial}{\partial t} \left[V_f \left(\rho_w S_w U_w + \rho_o S_o U_o + \rho_g S_g U_g \right) + V_v c_s U_s + V_r U_r \right]$$

$$= \sum_{k=1}^{n_f} \left[T_w \rho_w H_w \Delta \Phi_w + T_o \rho_o H_o \Delta \Phi_o + T_g \rho_g H_g \Delta \Phi_g \right] + \sum_{k=1}^{n_f} K \Delta T$$

$$+ \left[\rho_w q_{wk} H_w + \rho_o q_{ok} H_o + \rho_g q_{gk} H_g \right] + V \sum_{k=1}^{n_r} H_{rk} r_k + \left[H L_o + H L_v + H L_c \right]$$

$$+ \sum_{k=1}^{n_f} (H A_{CV} + H A_{CD})_k$$
(5A-8)

where, $\frac{\partial}{\partial t} \left[V_f (\rho_w S_w U_w + \rho_o S_o U_o + \rho_g S_g U_g) + V_v c_s U_s + V_r U_r \right]$ is the time-derivative of energy accumulation, U_w , U_o , U_g , and U_r refer to the internal energy for water, oil, gas, and rock respectively. The enthalpy of water, oil, and gas is represented as H_w , H_o , and H_g . $V \sum_{k=1}^{n_r} H_{rk} r_k$ refers to the energy reaction source term, where H_{rk} and r_k are the enthalpy and volumetric rate of reaction in layer k. HL_o is the total heat transfer rate, HL_v is the heat transfer rate for convection model, and HL_c is the constant heat transfer. The aquifer source term is described as $\sum_{k=1}^{n_f} (HA_{CV} + HA_{CD})_k$, where HA_{CV} and HA_{CD} are the respective rate of heat transfer via convention and conduction respectively. The energy term for flow between two regions is represented as $[T_w \rho_w H_w \Delta \Phi_w + T_o \rho_o H_o \Delta \Phi_o + T_g \rho_g H_g \Delta \Phi_g + K \Delta T]$ and the well source term for energy is shown as $[\rho_w q_{wk} H_w + \rho_o q_{ok} H_o + \rho_g q_{gk} H_g]$.

5.6 Nomenclature

Acronyms

AQ	Low salinity aquifer water
Ca^{2+}	Calcium ion
CMG	Computer Modeling Group
COOH	Carboxylic acid
cp	Centipoise
DIW	Deionzed water
DLVO	Derjaguin-Landau-Verwey-Overbeek
EOR	Enhanced Oil Recovery
FB	Formation brine
IFT	Interfacial tension
LSWI	Low salinity water injection
MIE	Multi-component ion exchange
md	Milli Darcy
Na^+	Sodium ion
PHREEQC	pH-Redox-Equilibrium in C language
Sor	Residual oil saturation
SW	Seawater
TAN	Total acid number

Variables and parameters

\mathbf{A}_{0}	Structural force coefficient
e	Electron charge
HACV	Respective rate of heat transfer via convention
HACD	Respective rate of heat transfer via conduction
Hi	Enthalpy of phase i ($j=g$, o, and w)
HLc	Constant heat transfer
HLo	Total heat transfer rate
HLv	Heat transfer rate for convection model
H _{rk}	Enthalpy rate of reaction in layer k
Κ	Equilibrium constant
k	Boltzmann constant
n _f	Number of neighboring regions or grid block faces
Р	Pressure
r _k	Volumetric rate of reaction in layer k
S	Saturation
Т	Temperature
Ti	Transmissibility in phase j (j=g, o, and w)
$\dot{ m V_{f}}$	Total fluid volume
V_{v}	Total void volume

Wi	Mole fraction of component i in the water
Xi	Mole fraction of component i in the oil
y i	Mole fraction of component i in the gas
Z	Valence of a symmetrical electrolyte solution

Greek letters

Permittivity
Zeta potential
Reciprocal Debye length
London wavelength
Decay length
Pore size distribution index
Reduced surface potential
Surface potential
Interaction potential
Contact angle
Disjoining pressure
Density

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Chapter 6 Summary, Conclusion, and Future

Work

LSWI and CO₂ LSWAG injection, as two economically and environmentally friendly EOR techniques, are capable of increasing oil recovery in secondary or tertiary recovery mode. Previous microscopic investigations using contact angle measurements to study wettability alteration by LSWI and CO₂ LSWAG injection exhibit inherent limitations of which the geochemical reactions cannot be fully captured, and one substrate allows only one measurement. To overcome this obstacle, a "displacement" method for measuring contact angle is proposed and studied with static conventional method and calculated value from disjoining pressure. On the macroscopic level, a shift in relative permeability curves is considered as an indicator for wettability alteration. The effect of injection temperature and different interpolation techniques to relative permeability curves in sandstone reservoir are further addressed with LSWI simulation. Finally, with the assumptions of using rock with no significant heterogeneity for measuring contact angle and residual oil saturation decreasing as wettability changes towards more waterwet, the microscopic contact angles are related to the macroscopic relative permeability curves for oil recovery prediction.

Chapter 2 presents a comprehensive literature review on CO_2 LSWAG injection and core-scale simulation study on hysteresis effect. Chapter 3 investigates three different approaches to relative permeability interpolation using Na⁺ concentration, Na-X equivalent fraction on exchanger, and porosity increase due to mineral dissolution. The effect of injection temperature is also investigated with respect to oil recovery, pH, and mineral dissolution/precipitation. Chapter 4 presents wettability studies using "displacement" contact angle measurements for LSWI and CO₂ LSWAG injection. The effect of Na and Ca cations, CO₂, and injection schemes including LSWI, CO₂ LSWAG injection and CO₂ + LSWI. Chapter 5 studies wettability through surface forces and disjoining pressure, as well as contact angles measured using conventional static and

displacement methods. The possibility of relating measured contact angle to relative permeability to model wettability alteration is explored and validated with oil recovery data from core flooding experiments. Finally, simplified screening procedures for obtaining an optimal brine concentration and composition are proposed, which can be more timesaving and cost-effective.

6.1 Conclusions

The major conclusions of this work are summarized as: (1) Effect of hysteresis in CO_2 LSWAG injection; (2) modeling effect of interpolation techniques and injection temperature in LSWI; (3) contact angle comparisons among the calculated value from disjoining, measured values from conventional and displacement methods; (4) using displacement contact angle measurements to study the effect of low salinity water, CO_2 , and injection schemes; (5) relation between contact angle and relative permeability.

(1) Effect of hysteresis in CO₂ LSWAG injection

• With incorporation of hysteresis effect into CO₂ LSWAG injection simulation, the optimum salinity obtained is 5000 ppm, instead of 2000 ppm (the lowest value in the range studied). This indicates the importance of including hysteresis effect in CO₂ LSWAG injection optimization as the optimum salinity might not always be the lower the better for obtaining higher oil recovery.

(2) Relative permeability interpolation techniques and temperature effect

 Injection temperature has significant impact on oil recovery in the sandstone block model used in this study. Injection temperature of 20°C results in 6-9% lower in oil recovery compared to injection temperature of 100°C. Lowering the injection water temperature appears to reduce the low salinity effect. Temperature has an impact on the equilibrium constant of aqueous chemical reactions and the reaction rate of mineral dissolution/precipitation. At lower temperature, the reaction rate of ion exchange on the rock surface and mineral dissolution due to LSWI is lower, which reduces the low salinity effect.

- The effect of interpolation techniques and parameter ranges used in this study has minor effect on oil recovery. However, the choice of interpolation techniques has noticeable effect on pH distribution and changes. The ion exchange interpolation approach results in the broadest range of pH increase and lowest oil recovery factor, indicating that pH value cannot be used as an evaluation for LSE; an increase in pH does not guarantee improved oil recovery by LSWI. There is no clear relationship between oil recovery factor and pH increase.
- Bicarbonate ions are found to have an influence on pH. With the effect of temperature, bicarbonate ions act as buffer for pH changes as LSW is injected into the reservoir block model.
- Calcite dissolution and dolomite precipitation occur near the injection well. In a basic environment, calcium concentration plays an important role in the calcite dissolution process. However, pH is not effective in this condition. A drastic decrease in calcium ions in injecting low salinity water results in calcite dissolution near the injector well, which further promotes the precipitation of dolomite.

(3) Contact angle comparisons

• Disjoining pressure can be used to characterize the expansion of EDL due to LSWI; however, chemical reactions like MIE effect are not covered. When only the intermolecular forces (van der Waals, electric double layer, and structural forces) are considered and chemical reactions like MIE are ignored during LSWI, the calculated value differ significantly from the measured values, indicating the effect of low salinity water is an interplay of both chemical reactions and expansion of electrical double layer.

- When comparing the contact angle measured using the displacement method versus the static conventional method, there is no noticeable difference for 2000 ppm NaCl since the energy barrier is the highest. A significant difference (approximately 9°) is observed for 2000 ppm CaCl₂. This is due to the additional pressure acting on the rock/brine and oil/brine interfaces, which could potentially accelerate the water film rupture process, leading to bridging of these interfaces through Ca²⁺.
- The displacement method for measuring contact angle better mimics the actual process compared to conventional static method and provide a more accurate outcome. In order to obtain an optimal salinity and composition for injection brine, as well as injection schemes for implementation, the displacement contact angle measurement can be used instead of conducting time-consuming core flooding experiments.
- The geochemical modeling showed that, compared with seawater, the 2000 ppm CaCl₂ LSW had a higher number of electrostatic bridges and oil surface species (-COOCa⁺) available for further binding if the equilibrium is disturbed. This indicates that the molality concentration of Ca²⁺ cation in the injection brine plays a more important role than the overall salinity. Simply decreasing salinity might not lead to a more water-wet condition, however, decreasing the concentration of Ca²⁺ might contribute to altering the rock wettability towards more water-wet.

(4) Displacement contact angle measurements

• The injection of 2000 ppm NaCl water alters the wettability towards slightly waterwet, and the injection of 2000 ppm CaCl₂ alters the wettability towards slightly oilwet. Low salinity water with divalent cation could increase the attraction forces between the rock/brine and oil/brine interfaces, promoting oil-wetness. However, low salinity with Na cation reduces the attraction forces, i.e., repulsive force increases, therefore, resulting in more water-wet.

- The deformation process during LSWI resembles the process of oil removal using surfactant. This "surfactant-like" behaviour lowers the interfacial tension and contributes to increased oil recovery. As CO₂ is introduced, due to the acidic effect of CO₂, it acts to wet the rock surface, leading to a more water-wet state. Therefore, the oil removal or oil drop deformation resembles the "roll-up" oil removal process.
- The injection of CO₂ promotes water-wetness and geochemical reactions between oil and brine. In the WAG process, more interactions between injection brine, CO₂ and pre-existing brine are expected, and this leads to different wettability alteration trend compared to CO₂ + LSWI. When NaCl LSW is used, continuous CO₂ + NaCl injection scheme is more efficient than WAG cycle of CO₂/NaCl in wettability alteration towards more water-wet. However, with CaCl₂ LSW, WAG cycle of CO₂/CaCl₂ can alter the rock wettability to more water-wet compared to continuous CO₂ + CaCl₂ injection.

(5) Relation between contact angle and relative permeability curves

• With the assumption of surfaces with no significant heterogeneity and residual oil saturation decreases as the rock wettability changes from oil-wet to water-wet, the measured contact angles can then be used to model wettability alteration and oil recovery prediction by linking them to relative permeability curves. The errors between the modeling and experiments are within an acceptable range (less than 6%).

6.2 Recommendations for Future Work

Based on the literature review and results obtained in this thesis, the following are recommended for potential future work.

- Review of the simulation studies suggested two effects for CO₂ LSWAG injection. One is that LSWI could potentially compensate for the delayed production by CO₂
 WAG injection in the early stage, and the injection of CO₂ promotes ion exchange and geochemical reactions for LSWI due to its reaction with water and calcite minerals. The other effect is that fines migration, and subsequent water blockage induced by fines plugging, divert the flow path to unswept low permeability zones. Due to the lack of experimental evidence, more laboratory experiments, especially pore-scale studies, are recommended to investigate the driving forces and mechanisms for improved oil recovery by CO₂ LS WAG injection.
- Development of a more reliable CO₂ LSWAG injection model is necessary, considering geochemical interactions of the crude oil/brine/rock, three-phase relative permeability, capillary pressure, and hysteresis effect.
- For the modeling study, we only studied one salinity (5000 ppm) for injected low salinity water and the volume fraction of calcite is considered same in all layers. Moreover, it is found that there exists calcite dissolution and dolomite precipitation near the injector with a relatively low initial calcite volume fraction (0.02). Thus, it would be important to further investigate the effect of different salinities and concentrations of potential determining ions (Na⁺, Ca²⁺, or Mg²⁺), as well as reservoirs with different mineralogy, such as an upward fining of calcite cement
- For the contact angle measurements, all are conducted at ambient condition. The effect of temperature and pressure is not considered. As the temperature and pressure exceeds the critical point for CO₂, the state of CO₂ will become supercritical, with properties midway between a gas and a liquid. Therefore, in order to better understand the wettability alterations with supercritical CO₂, more research with respect to elevated temperature and pressure should be carried out in the future.

If wettability alteration is considered as the main mechanism for LSWI or CO₂ LSWAG injection, this displacement contact angle measurement which mimics the real reservoir displacement process could be used as a preliminary screening for brine concentration and composition, as well as injection schemes. However, to achieve a systematic evaluation process, more experimental data with respect to temperature and pressure are required.

• In our study, we linked the measured contact angle to relative permeability and validated the proposed wettability alteration model with limited experimental data. More experimental research is needed to further explore the relationship between contact angle, brine salinity and composition, and surface functional groups.