

Review

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

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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



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1. Introduction

Maximizing oil recovery from existing reservoirs plays a significant role in increasing profitability and sustainability of the oil and gas industry. Generally, oil recovery processes are classified as primary, secondary, and tertiary. In primary recovery, oil production comes from natural energy present in the reservoir. As the reservoir pressure reduces and oil production declines, secondary recovery is implemented, typically with waterflooding, to displace oil towards production wells. To achieve higher oil production, tertiary recovery, also known as enhanced oil recovery (EOR), is implemented. 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 [1] 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. Moreover, as the concerns for climate change continue to increase and the petroleum industry is positioned to deal with this challenge, finding an EOR method that is both technically and economically feasible and addresses the environmental concerns is of great importance.

The chemical EOR economic evaluation conducted by Al-Murayri et al. [2] 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 [3,4]. 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 [5–8]. 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 [6,7,9] 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 [10,11], 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 CO₂ 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, CO₂ WAG injection and CO₂ LSWAG injection. The fundamentals of CO₂ WAG injection and LSWI in sandstone and carbonate are presented, including basic theory and mechanisms. Laboratory studies of CO₂ 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 CO₂ LSWAG injection are addressed along with identified research gaps. In the end, to fill the void of the hysteresis study on CO₂ 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. Bibliometric Study

This literature review on CO₂ LSWAG injection is defined and constrained as the following, with the goal of identifying materials focusing on CO₂ WAG in injection, LSWI, and CO₂ LSWAG injection. Sources are constrained to Google Scholar and OnePetro.

CO₂ WAG Injection. Theory and working mechanisms.

LSWI. Mechanisms in both sandstone and carbonate are included.

CO₂ LSWAG Injections. Both laboratory and simulation studies are documented. Specific considerations are given to the effect of different parameters in experimental studies and simulation studies aiming to fully capture the effect of CO₂ and low salinity water.

2.1. Identification and Filtering

Searches are conducted according to the defined constraints using the listed sources. The documents which are identified as relevant are downloaded and reviewed for applicability filtering.

2.2. Discussion of Relevant Literature

Through the identification and filtering process, relevant literature has been selected and reviewed in detail. The findings are categorized based on the following hierarchy:

- CO₂ WAG injection
 - ❖ Miscible and immiscible process
 - ❖ Hysteresis effect
- LSWI
 - ❖ Mechanisms in sandstone
 - ❖ Mechanisms in carbonate
- CO₂ LSWAG injection

- ❖ Experimental studies and effect of different parameters
 - Miscibility
 - CO₂ solubility
 - Brine salinity and composition
 - Rock composition
 - WAG parameters
 - Wettability
 - Pressure and temperature
- ❖ Simulation studies
 - Core scale
 - Field scale

Findings from the literature review can be found in the following Sections 3–5.

3. 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 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) [12]:

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

If the mobility ratio is less than or equal to 1 ($M \leq 1$), 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 [13] and Perera et al. [14] listed the characteristics which enables CO₂ to remove oil from the reservoir effectively (Figure 1), including the effect of CO₂ physical and chemical characteristics on oil phase, brine phase and reservoir rock. CO₂ 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 [15]. This acidic effect also contributes to the stabilization of negatively charged clay particles [16].

Generally, during a CO₂ WAG injection process, utilization of CO₂ can achieve enhanced oil recovery through either miscible or immiscible process. The development of miscibility between injected CO₂ 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 C₇₊ fraction) [17].

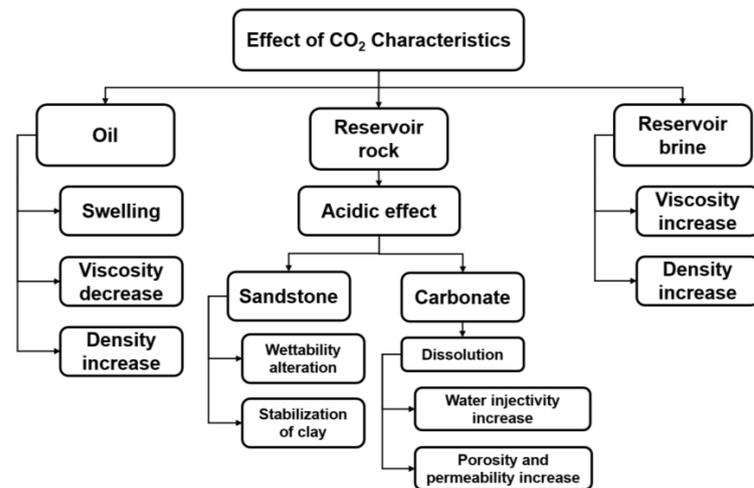


Figure 1. Effect of CO₂ physical and chemical characteristics on oil/brine/rock.

3.1. Miscible Process

In the oil recovery process of gas injection, the injected gas will develop first contact or multiple contact miscibility with the oil [14]. 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 CO₂ [18].

Among the factors that affect CO₂ miscibility in oil, pressure of the reservoir is the most important and a key parameter for determining miscibility [19,20]. Generally, miscibility between CO₂ and reservoir oil is achieved with pressure above the minimum miscible pressure (MMP). The CO₂ miscible process is illustrated in Figure 2, showing a transition zone, miscible with the forefront reservoir oil and the injected pure CO₂ near injection well. Jarrell et al. [21] demonstrate a development of transition zone with no interface by the mass transfer between reservoir oil and CO₂. Two processes are considered as the miscibility development of CO₂ with reservoir oil: (1) condensing gas drive; and (2) vaporizing gas drive. In the former process, the injected CO₂ dissolves into the reservoir oil, forming dynamic miscibility. In the latter process, reservoir oil component with intermediate-to-high molecular weight vaporizes into CO₂, and form miscibility under certain conditions.

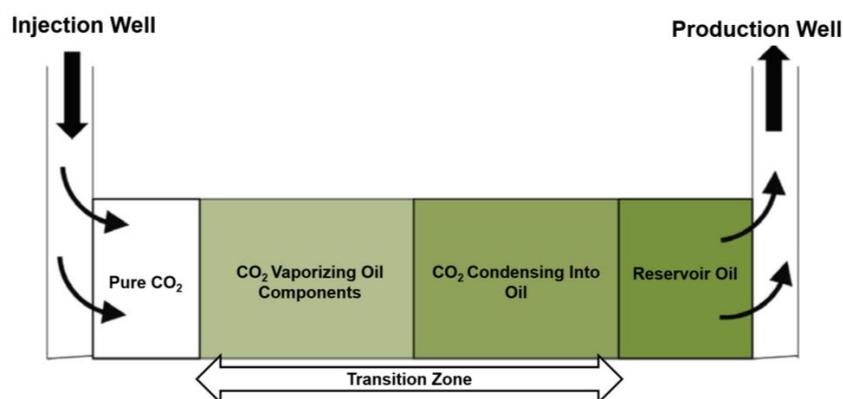


Figure 2. Schematic CO₂ miscible process (adapted from Verma [18]).

3.2. Immiscible Process

CO₂ 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) [18]. Under these circumstances, CO₂ and oil will not form a single phase. With immiscible CO₂ WAG injection,

improved oil recovery is achieved by oil swelling and viscosity reduction induced by dissolution of CO₂ into reservoir oil. Thus, CO₂ solubility in the reservoir oil is a key factor for effective implementation of immiscible CO₂ WAG injection. CO₂ solubility in oil can be affected by saturation pressure, temperature of the reservoir, and composition of oil [22,23]. As pressure increases or temperature decreases, CO₂ solubility in oil increases. However, as the temperature is lower than CO₂ critical temperature, CO₂ solubility is also affected by oil composition and liquefaction, where gaseous CO₂ is more soluble in crude oil than liquid CO₂ [24–26]. Commonly recognized oil recovery mechanisms for the immiscible CO₂ displacement process include oil swelling and viscosity reduction [27–30], IFT reduction [31,32], and blowdown [13,31,33].

3.3. 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 [34]. Generally, the three-phase hysteresis effect is more pronounced in immiscible WAG process than miscible WAG process [35] and its impact is more significant with non-wetting phase (gas) than wetting or intermediate wetting phase [36].

4. Low Salinity Water Injection (LSWI)

Low salinity effect (LSE) was first discovered by Bernard [37] 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 [38–54].

4.1. 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 [55]. Figure 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.

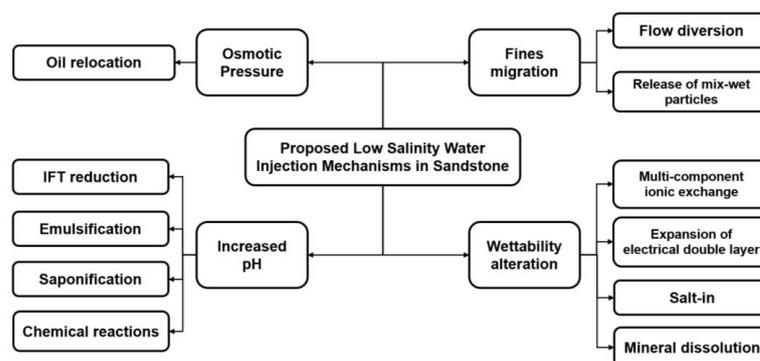


Figure 3. Overview of some proposed mechanisms of LSWI in sandstones.

Fines migration can be induced by the poorly cemented clay minerals [56] or release of mix-wet particles [41]. 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 [41,57]. In situ increase in alkalinity [58] arising from the differences in cation affinity to negatively charged surface [59] gives rise to IFT reduction, surfactant-like behavior and chemical reactions for oil detachment [58,60]. 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 [61–65]. Additional oil recovery by LSWI is often observed with wettability alteration towards more water-wet [50,66–69]. The proposed mechanisms related wettability alteration are multi-component ionic exchange (MIE) [70,71], expansion of electrical double layer [47,72,73], salt-in effect [53], and mineral dissolution [74]. For a detailed review and discussion on the mechanisms, readers can refer to the work conducted by Sheng [3], Rezaeidoust et al. [53], Katende and Sagala [75], Al-Shalabi and Sepehrnoori [76], and Yue et al. [77].

4.2. 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 [78,79]. 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 4) [76,80–82].

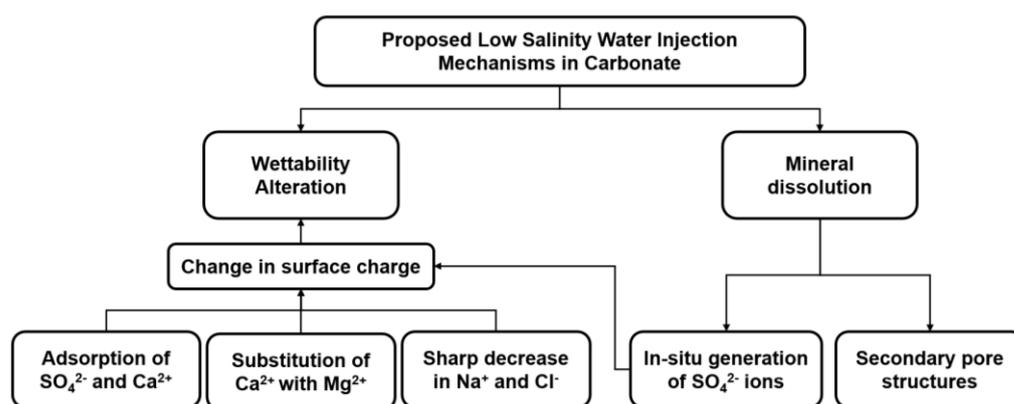


Figure 4. Summary of proposed mechanisms of low salinity water injection in carbonates.

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 [83–85]. 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, [86,87], 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 [88,89]. Low salinity water with a significant reduction in the concentrations of Na^+ and Cl^- is the key to trigger wettability alteration in carbonate reservoirs [54,82,88].

Mineral dissolution. Mineral dissolution during flooding could result in secondary pore structure and potentially expelling of oil [76]. 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 [82,90].

5. CO₂ LSWAG Injection

Based on the review on LSWI and CO₂ WAG injection, it is possible to combine the strength of these two methods to alter wettability and enhance CO₂ mobility; thus, increasing oil displacement efficiency. A comprehensive review of CO₂ LSWAG laboratory and simulation studies has been completed; it is presented accordingly with proposed mechanisms and environmental aspects of CO₂.

5.1. 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. Table 1 summarizes the experimental data from literature.

Most results confirmed improved oil recovery using this hybrid technique, in both secondary and tertiary modes, with some exceptions [10,11]. 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 [66,67]. Moreover, the salinity of injection water adopted in the core flooding experiments by Jiang et al. [11] is 10,000 ppm, which lies beyond the range suggested for LSWI (1000–5000 ppm) [58]. 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 CO₂ in brine, and wettability alteration on oil recovery enhancement are reviewed and discussed in this section.

Table 1. Summary of CO₂ Low Salinity WAG Injection Laboratory Experiments.

Ref ¹	Rock Properties				Fluid Properties			Test Temp ⁶ [°C]	WAG Process					Total RF ¹³ [%]	CO ₂ LS WAG Injection Performance
	Type	Aging	Φ ² [%]	K ³ [mD]	Oil	FB ⁴ [ppm]	IB ⁵ [ppm]		Type	Mode	Cycle	Slug [PV]	Ratio		
[11]	Berea sandstone	1.5 days @ 60 °C	19.4–20.3	60.7–99.2	Crude Oil 7.92 cp	30,000	10,000–32,000	60	MW ⁹	T ⁷	6	0.5	1:1	52–60	<ul style="list-style-type: none"> In tertiary CO₂ WAG injection, oil recovery increased slightly with the increasing injection brine salinity, however, the difference is not very significant
[91]	Outcrop limestone (71.6% calcite)	No aging	29	90	Crude oil	0 6000 20,000	0 6000 20,000	49	MW	S ⁸	N/A	0.33	1:1	74–92	<ul style="list-style-type: none"> Lower salinity leads to higher CO₂ dissolution in water, resulting in higher oil recovery Better displacement efficiency is achieved with CO₂-water mixture compared to continuous CO₂ injection
[7]	Sandstone Kaolinite-free	2 days @ 70 °C	29–32	333–357	Heavy oil 6.5% asphaltene 10.1 cp and 0.89 g/cm ³ @ 96 °C	50,000	1000 50,000	50	LS 12-IMW HS 11-IMW	S	5	0.16	1:1	74–92	<ul style="list-style-type: none"> In secondary mode, 5% increase in oil recovery is observed in LS WAG injection compared to LSWI CO₂ effectively improved oil recovery in heavy oil using LS WAG injection
[9,92]	Berea Sandstone	14 days @ 91 °C	12	0.63	Crude oil 0.87 g/cm ³	100,000	25,679 12,840 1027	91	IMW ¹⁰	S, T		S: LSWI T: Immiscible CO ₂ flooding		81.5	<ul style="list-style-type: none"> LSWI produced significant additional oil and the CO₂ injection after LSWI further improved oil recovery Injection of CO₂ altered wettability of sandstones towards water-wet
[10]	Outcrop Grey Berea sandstone 6% Kaolinite and 2% Illite	No aging	17.6–19.1	62–79	Dead crude oil 0.82 g/cm ³	174,156	54,680 5000	65	MW	S	3	2.6–8.2	1:1	61.7–64.6	<ul style="list-style-type: none"> CO₂ WAG injection produced more oil than water flooding The salinity of injection brine had great impact on the rock wettability alteration
[93]	Reservoir carbonate	No aging	N/A ¹⁴	N/A	Crude oil 3.08 cp and 0.85 g/cm ³ @ 25 °C	163,000	5000	121	MW	S	2	0.2	1:2 1:2 2:1	58–88	<ul style="list-style-type: none"> LSE is observed with WAG ratio of 1:2 and 2:1. However, no LSE is seen using WAG ratio of 1:1 Due to the design with no salinity shock for each core flooding experiments, the EOR effect of CO₂ LS WAG injection is mainly attributed to the higher dissolution of CO₂ in LSW
[94]	Berea sandstone	No aging	17–18.5	143–156	Crude oil (Van Gogh)	5000	5000 4000 3000 2000 1000	71	MW	S	6 3 2	0.2 0.4 0.6	1:1	40–55	<ul style="list-style-type: none"> Results from RSM indicates that slug size of 0.45 PV and NaCl salinity of 4313 results in highest oil recovery in this case
[95]	Reservoir sandstone (with clay)	1 day @ 80 °C	N/A	N/A	Crude oil 0.82 g/cm ³	104,000	13,480	50	IMW	S	3	0.5	1:1	68	<ul style="list-style-type: none"> Depleting NaCl in brine improved oil recovery

Table 1. Cont.

Ref ¹	Rock Properties				Fluid Properties			Test Temp ⁶ [°C]	WAG Process					Total RF ¹³ [%]	CO ₂ LS WAG Injection Performance	
	Type	Aging	Φ ² [%]	K ³ [mD]	Oil	FB ⁴ [ppm]	IB ⁵ [ppm]		Type	Mode	Cycle	Slug [PV]	Ratio			
[96]	Bentheimer sandstone (0.5% Kaolinite) Berea sandstone (2% Kaolinite)	No aging	22.4–22.9	94–207	Light crude oil 3.58 cp and 0.83 g/cm ³	19,751	36,170 3360	60	HS-MW LS-MW	T	N/A	0.2	1:1	65.2–85.2	<ul style="list-style-type: none"> LSW as secondary mode and miscible CO₂ WAG as tertiary mode is effective in Berea cores No LSE is observed in Bentheimer cores 	
[97]	Berea sandstone	No aging	20.6–21.1	88.6–90.4	Light Oil (Oman field)	50,000	5000 (NaCl) 5000 (MgCl ₂) 5000 (KCl)	60	IMW	T	3	0.5	1:1	45–55.4	<ul style="list-style-type: none"> LSE is observed in all three CO₂ LS WAG injections The dominant mechanism behind EOR of CO₂ LS WAG injection is a combination of wettability alteration by MIE of Na⁺ ions and oil swelling and viscosity reduction by CO₂ dissolution in oil 	
[98]	Reservoir sandstone	35 days @ 90 °C	14–17	1–5	Crude oil (Bartlesville) 600 cp and 0.83 g/cm ³ @ 25 °C	104,000	51,400 5140	50	MW	S, T	1. 16 PV SW + 10 PV miscible CO ₂ 2. 8 PV SW + 8 PV LSW + 10 PV miscible CO ₂ 3. 6 PV LSW + 10 PV miscible CO ₂			30–90	<ul style="list-style-type: none"> The solubility of CO₂ in smart seawater was found to be reduced, and the lowest solubility was when NaCl was depleted and Ca²⁺ was diluted 5 times. Smart water with depletion of NaCl and dilution of Mg²⁺ or SO₄²⁻ resulted in higher oil recovery 	
[8]	Sandpack (6% Kaolinite)	No aging	31.7–33.5	690–810	Crude oil 5.1 cp and 0.85 g/cm ³ @ 50 °C 2.7 cp and 0.83 g/cm ³ @ 80 °C		0 1000 2000 3000 4000	50 80		S, T	1. 2 PV initial brine solution + 0.3 PV CO ₂ slug + 2.7 PV chase brine solution 2. 1/2/3 PV initial brine solution + 0.3 PV CO ₂ slug + 3.7/2.7/1.7 PV chase brine solution			46–58	<ul style="list-style-type: none"> The use of saline solutions leads to salting out of CO₂ and very little CO₂ was dissolved The use of saline solutions decreased CO₂ adsorption rate in the solution The use of LSW (1000 and 2000 pm) is recommended in combination with CO₂ injection for EOR 	
[99]	Carbonate Calcite (52.8%) Dolomite (16.6%)	28 days @ 90 °C	18	26–30	Crude oil 13 cp and 0.88 g/cm ³ @ 22 °C	183,700	13,090 1309	90	IMW	T	N/A		0.4	1:1	68.2	<ul style="list-style-type: none"> LSW gives 8.2% higher oil recovery compared to CO₂ SW WAG injection Higher solubility of CO₂ in LSW promotes oil mobilization through wettability alteration towards more water-wet and minimizing difference between the oil-water density

¹ reference; ² porosity; ³ permeability; ⁴ formation brine; ⁵ injection brine; ⁶ temperature; ⁷ tertiary recovery mode; ⁸ secondary recovery mode; ⁹ miscible WAG injection; ¹⁰ immiscible WAG injection; ¹¹ high salinity; ¹² low salinity; ¹³ recovery factor; ¹⁴ not mentioned.

5.1.1. Effect of Miscibility

Based on a WAG injection field review by Christensen et al. [100], 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. [101] 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 [4,101]. Up to date, only one study was found on the investigation of miscibility effect during CO₂ LS and HS WAG injection. Kulkarni et al. [102] 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 CO₂ is used as the injection gas under miscible and immiscible conditions. Their results, shown in Table 2, indicate that miscible CO₂ 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 CO₂ miscibility with oil, and LSW might not play a role for improving oil recovery [103].

Table 2. Oil recovery comparison between miscible and immiscible WAG injection [102].

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%

5.1.2. Effect of CO₂ Solubility in Brine

Previous experimental and modeling studies demonstrate that CO₂ solubility in brine increases with decreases in salinity [9,104–106]. This increment of CO₂ solubility with low salinity water can result in improved oil recovery through CO₂-brine IFT reduction [9]. Bennion and Bach [107] 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. [108] 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. [7], 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. [8] 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 [8]. A small part of the gas molecules reacts with water, and the following reactions will take place to produce carbonic acid (H₂CO₃) and HCO₃⁻ and CO₃²⁻ ion.





The CO_2 molality, moles of CO_2 absorbed in a solvent, as a function of salinity is depicted in Figure 5, showing that CO_2 absorption decreases with increasing salinity and temperature, and decreasing pressure.

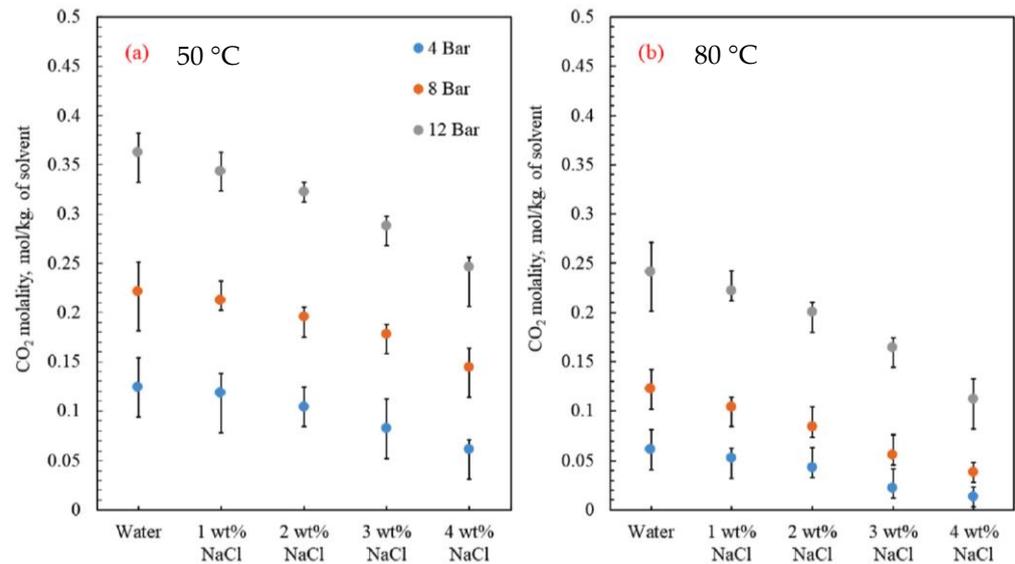


Figure 5. CO_2 molality results for different salinities (0–4 wt% NaCl); (a) 50 °C; (b) 80 °C [8].

They used the Young-Laplace equation of capillarity to calculate the IFT between CO_2 and brine [109]. As shown in Figure 6, the interfacial tension of brine and CO_2 decreases with decreasing salinity and increasing temperature and pressure. Chaturvedi et al. [8] claimed that the decrease in IFT is ascribed to the increasing CO_2 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 CO_2 LS WAG core flooding experiments recommended the use of low salinity water (1 and 2 wt% NaCl) in conjunction with CO_2 injection to improve oil recovery [8].

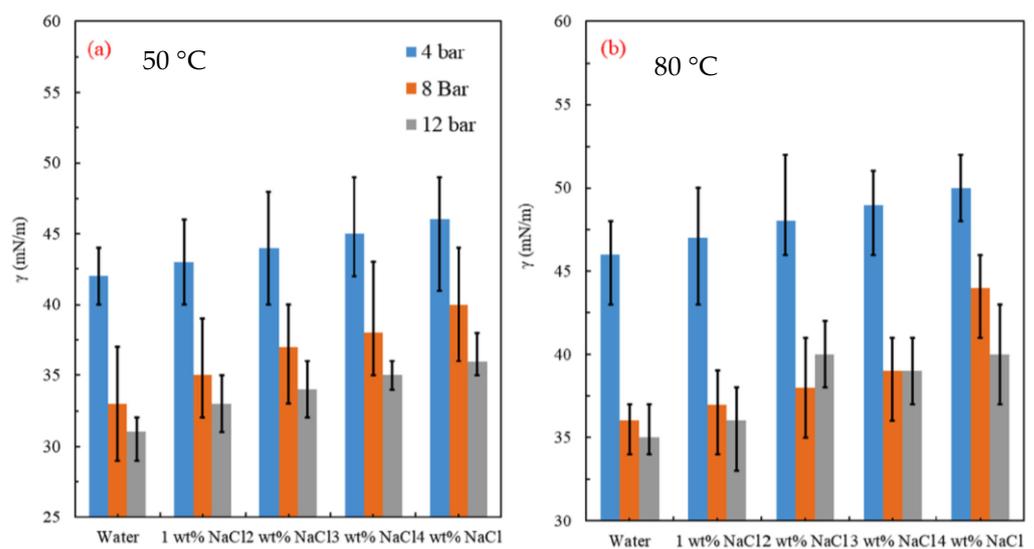


Figure 6. CO_2 – brine solution interfacial tension at different pressures (4–12 bar) and temperature of (a) 50 °C; (b) 80 °C [8].

5.1.3. 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 [40,42,110,111]. Jiang et al. [11] 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 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, 16,000, and 32,000 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. [70] 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 [58].

On the other hand, Zolfaghari et al. [7] 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 50,000 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. [60], 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.

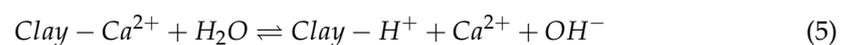
AlQuraish et al. [96] investigated CO₂ low salinity (LS) and high salinity (HS) WAG injection as tertiary recovery to explore the effect of salinity and brine composition. In their study, synthetic formation water at 20 wt% salinity, seawater (acting as high salinity water, HSW), and 10-time diluted seawater (acting as low salinity water, LSW) were used as the aqueous phase. Detailed information of the brine compositions can be found in Table 3. 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.

Table 3. Composition of brine [96].

Parameter	FB ¹ Formation Brine	HSW ² Seawater	LSW ³
Calcium, mg/L	28,035.05	522	51
Magnesium, mg/L	5241.18	1624	140
Sodium, mg/L	51,809.52	13,416	1220
Potassium, mg/L	-	507	45
Chloride, mg/L	112,365.25	23,321	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	3360
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

¹ formation brine; ² high salinity water; ³ 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 4) was studied by Al-Saedi et al. [95]. Their results (Table 5) (¹ formation brine; ² seawater; ³ modified seawater; ⁴ without NaCl; ⁵ without NaCl and 5-time diluted Ca²⁺; ⁶ without NaCl and 5-time diluted Mg²⁺; ⁷ without NaCl and 5-time diluted SO₄²⁻) 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 [98], resulting in more desorption of oil from the negatively charged surfaces.

**Table 4.** Composition of the formation and injected brine [95] (mg/L).

Compound	FB ¹	SW ²	SW -0NaCl ⁴	MSW1 ³ 0NaCl-d ₅ Ca ⁵	MSW2 0NaCl-d ₅ Mg ⁶	MSW3 0NaCl-d ₅ SO ₄ ⁷
NaCl	81,000	25,000	0	0	0	0
CaCl ₂	17,000	2000	2000	400	2000	2000
MgCl ₂	5000	10,500	10,500	10,500	2100	10,500
Na ₂ SO ₄	-	4900	4900	4900	4900	980
KCl	1000	-	-	-	-	-
TDS	104,000	43,400	18,400	15,800	9000	13,480

¹ formation brine; ² seawater; ³ modified seawater; ⁴ without NaCl; ⁵ without NaCl and 5-time diluted Ca²⁺; ⁶ without NaCl and 5-time diluted Mg²⁺; ⁷ without NaCl and 5-time diluted SO₄²⁻.

Table 5. Recovery factor of different flooding sequences [95].

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 PV CO 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

Even though these modifications are conducted on seawater, these results suggest that it might be possible to achieve higher oil recovery in CO₂ LSWAG injection with the manipulation of ion compositions and WAG process is more efficient compared to modified seawater and continuous CO₂ injection. It can be inferred that further dilution of Ca²⁺ or depleting Ca²⁺ in LSW might improve oil recovery even more when injected alternatively with CO₂.

Al-Abri et al. [97] 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 5000 ppm NaCl and highest in 5000 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.

5.1.4. Effect of Rock Composition

AlQuraish et al. [96] 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 6). 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 [41] and pore scale [57] suggested that the migration of fine particles (especially kaolinite) might be a contributor to improved oil recovery in sandstones.

Table 6. Comparison of total recovery for Berea and Bentheimer core samples [96].

Rock Type	Description of Experiment	Total Recovery %OOIP
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

Zolfaghari et al. [7] 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. [112], fines migration was reported to play an insignificant role. Further investigations are required to better understand the roles of clays in CO₂ LSWAG injection.

5.1.5. 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. [94] 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. [6] conducted robust optimization on CO₂ LSWAG injection under geological uncertainties [113] 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 [114,115] 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. [93] 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 7. WAG ratio 1:2 yields the highest oil recovery and WAG ratio of 2:1 results in the 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. [6].

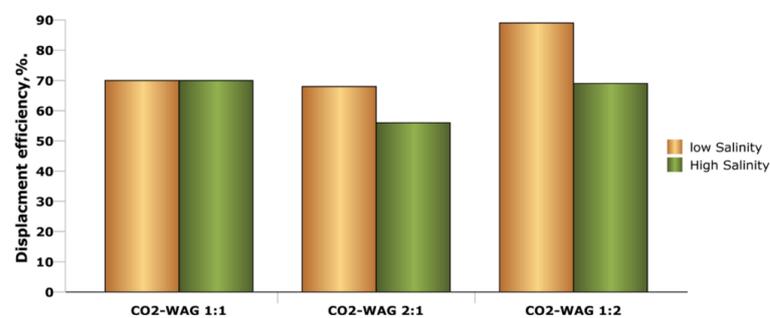


Figure 7. Effect of WAG ratios on oil recovery in CO₂ HS and LS WAG injection [93].

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. [116] performed miscible CO₂ WAG optimization using stochastic algorithm 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. [117] 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 [118]. 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 [119–121] and most field applications [4,100] 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.

5.1.6. Effect of Wettability

According to Anderson [122], 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. [9] performed contact angle measurements between reservoir sandstone core discs to mimic a condition of miscible

CO₂ flooding with seawater and low salinity water (Figure 8). The measurement condition A, B, and C are described in Table 7.

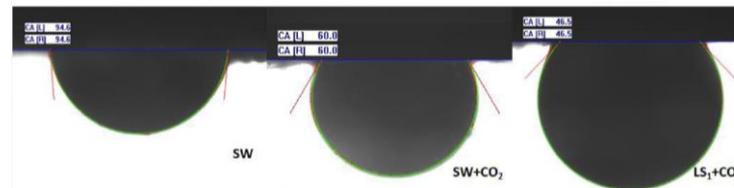


Figure 8. Contact angle between sandstone and oil-droplet at conditions A, B, and C [9].

Table 7. Measurement condition A, B and C [9].

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 CO ₂ for 2 days Seawater and CO ₂ 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 CO ₂ Low salinity water and CO ₂ is between the disc and oil-droplet during contact angle measurement

As brine salinity decreases, the solubility of CO₂ increases, forming in situ carbonated water of higher CO₂ saturation in the brine phase. This leads to IFT reduction and wettability alteration of rock towards hydrophilic; hence, improved oil recovery [9]. Similar results were observed from Almeida da Costa et al. [123]. 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 9, the IFT between crude oil and CO₂ decreases with increasing pressure, indicating enhanced molecular interactions, and also contributes to increased oil mobility [123]. 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.

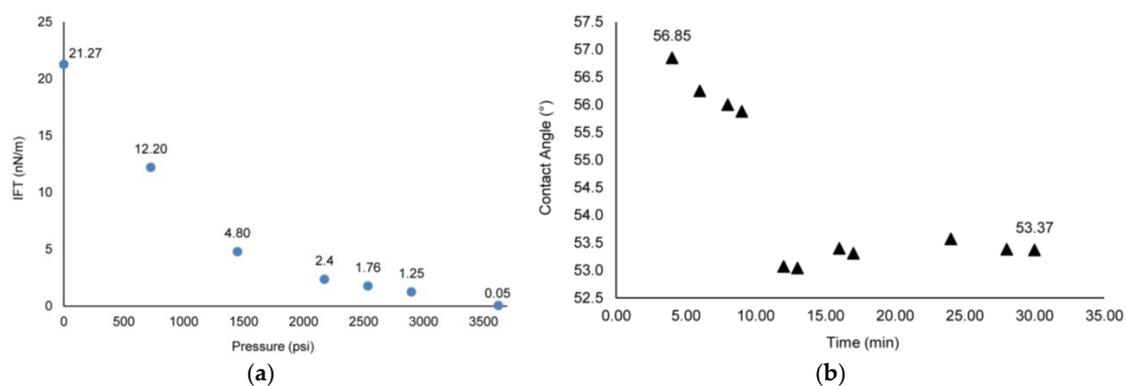


Figure 9. (a) IFT of crude oil/CO₂; (b) Contact angle as a function of time and pressure in a low salinity brine/CO₂ system at 60 °C (adapted from Almeida da Costa et al. [123]).

Al-Abri et al. [97] investigated the wettability alteration by CO₂ LS WAG injection based on the calculated wettability index (WI) from contact angle measurements. The definition of WI is defined as

$$WI = \frac{\theta_{original} - \theta_{final}}{\theta_{original} - \theta_{initial}} \quad (6)$$

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 8. 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 8, samples 3, 5 and 7). Moreover, as CO₂ is incorporated into low salinity water, the wettability index increased and the final contact angle decreased (Table 8), indicating the alteration of wettability towards more water-wet. They also conducted three tertiary CO₂ LS WAG core flooding experiments with high salinity flooding as secondary recovery. The lowest oil recovery (43.5%) was obtained in the combined injection of CO₂ and KCl brine, which has the lowest wettability index. This suggests that the wettability alteration by the interactions between LSW, CO₂ and rock minerals could be one of the contributors to improved oil recovery.

Table 8. Value of contact angle and wettability index [97,123].

Sample No.	Brine	$\theta_{initial}$	$\theta_{original}$	θ_{final}	WI
1	HS ¹ (50,000 ppm)	51.24	118.19	71.43	0.70
2	HS (50,000 ppm)—CO ₂	51.24	114.33	42.12	1.14
3	NaCl (5000 ppm)	51.24	133.85	36.44	1.18
4	NaCl (5000 ppm)—CO ₂	51.24	118.78	33.34	1.27
5	KCl (5000 ppm)	51.24	109.45	41.95	1.16
6	KCl (5000 ppm)—CO ₂	51.24	122.33	43.58	1.11
7	MgCl ₂ (5000 ppm)	51.24	126.21	52.37	0.98
8	MgCl ₂ (5000 ppm)—CO ₂	51.24	101.23	35.26	1.32

¹ high salinity brine.

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 CO₂/brine/oil system by Ameri et al. [124] showed that wettability of the substrate was altered from strongly water-wet to a less water-wet state with decreasing salinity (Figure 10). Their results disagree with that of Teklu et al. [9], 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. [125] 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. [9] and Al-Abri et al. [97]. 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.

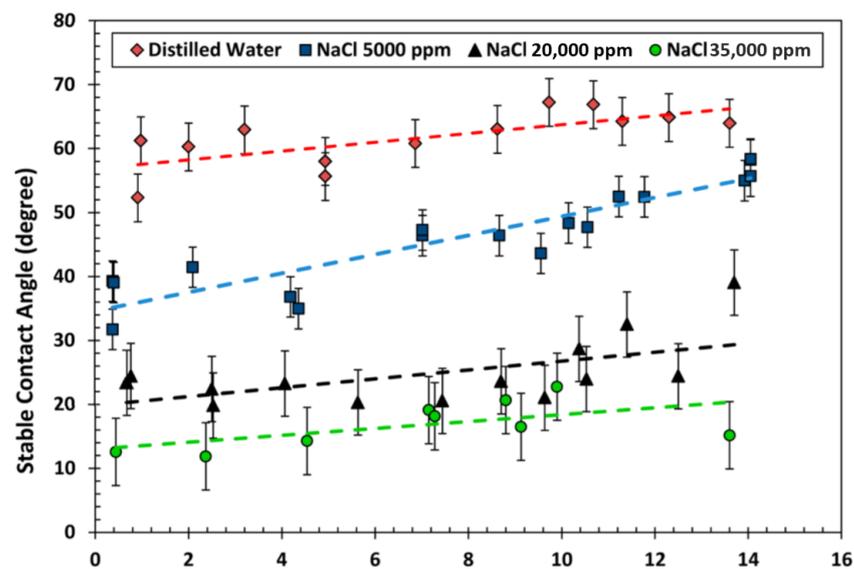


Figure 10. Contact angle measurements for sandstone after being saturated with oil, brine and CO₂ at 45 °C [124].

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. [126] 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.

5.1.7. Effect of Pressure and Temperature

During a CO₂ LSWAG injection, pressure determines whether CO₂ remains miscible or immiscible with the reservoir oil [19,20]. For a certain reservoir, as discussed in Section 5.1.1, with pressure higher than MMP, higher oil recovery is expected compared to the scenario with low pressure which is below MMP. Pressure and temperature could also affect the solubility of CO₂ in oil and water and the interfacial tension of CO₂-brine, CO₂-oil, and oil-brine [8,123]. These effects have been discussed in Sections 5.1.2 and 5.1.6. However, investigations on the overall effect of pressure and temperature on CO₂ LSWAG injection are very limited.

Chaturvedi et al. [8] investigated increased oil recovery due to CO₂ LSWAG injection in sand-packs at temperature of 323 K and 353 K (Figure 11). The salinities of the injected NaCl brine are from 0 to 4 wt% NaCl. It is seen that with 0–1 wt% NaCl injection brine, oil recovery increases with injection temperature. However, with 2–5 wt% NaCl injection brine, oil recovery decreases with increasing temperature, from 323 K to 353 K.

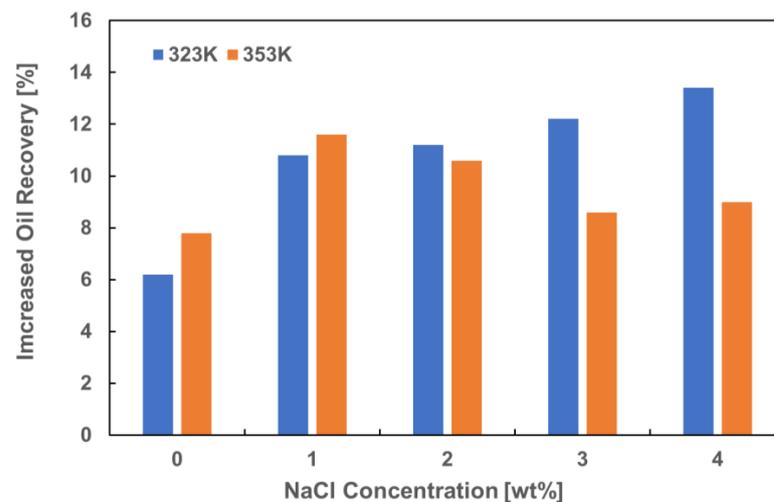


Figure 11. Oil recovery of core flooding experiments in sand-packs with CO₂ LSWAG injection at test temperature of 323 K and 353 K (adapted from Chaturvedi et al. [8]).

5.2. 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 [127–130], relative permeability, capillary pressure [35,36,128,130–134], petrophysical properties [130,135,136], and miscibility [35,36,130,133,137,138], have been investigated. However, only a few modeling [134,139–142] 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 [134], salinity of a specific aqueous component [143], equivalent fraction of a specific aqueous component on the exchanger [140–142,144], or porosity changes induced by mineral dissolution. Fjelde et al. [139] 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 intra-aqueous reactions, ionic exchange, and mineral dissolution/precipitation should be incorporated into the simulator.

Preliminary modeling of the CO₂ LSWAG hybrid process was initiated by Dang et al. [6] and followed by Naderi and Simioo [111] and Nguyen et al. [145]. Dang et al. [6] first performed simulations in a 1-dimensional heterogeneous reservoir and then upscaled to a field scale. They used the model from Nghiem et al. [146] to simulate the CO₂ flooding process considering CO₂ dissolution in oil and water, and models from Dang et al. [142,144] 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 [6]. Wettability alteration by LSWI is modeled with relative permeability curves shifting towards more water-wet. Their results [6] 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 12). 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 [111] 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.

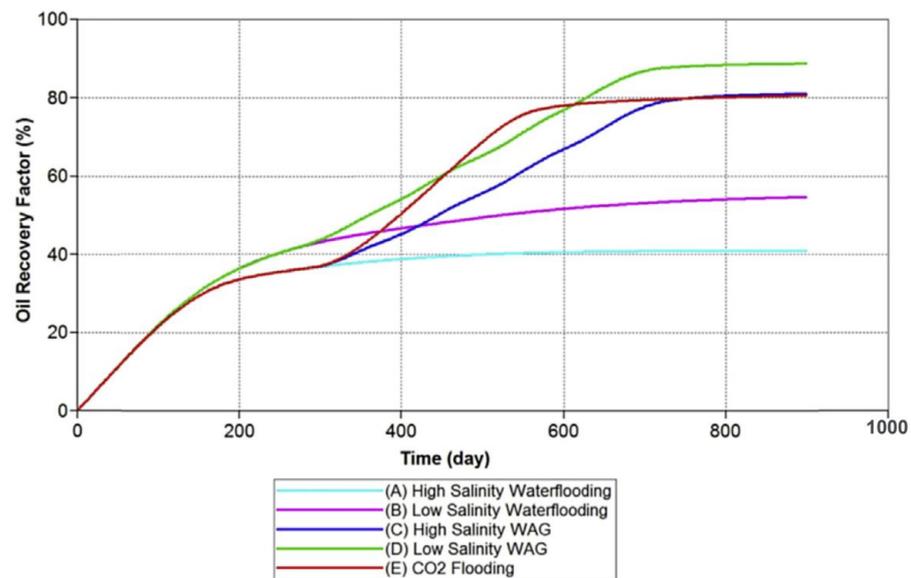


Figure 12. Cumulative oil recovery of different cases [6].

Subsequently, Nguyen et al. [145] modeled fines transport (fines deposition, migration, and plugging) using the approach from Gorucu et al. [147] and investigated the role of fines transport while integrating it with wettability alteration and geochemical reactions. Fines transport is considered in LSWI as follows:

$$\frac{\partial V_t}{\partial t} = \beta_1 c_f^k - \beta_2 V_{depo}^k (v_{iw} - v_{cr}) + \beta_3 (1 + \beta_4 V_t^n) v_{sw} c_f^k \quad (7)$$

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 [57,148]. 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 13 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 CO₂ flooding (mid-2007 to 2020) and (ii) high-salinity (HS) flooding followed by CO₂ 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 CO₂ flooding, since fines plugging blocked the high permeability porous media, CO₂ invades low permeability zones and recovery includes previously untouched residual oil.

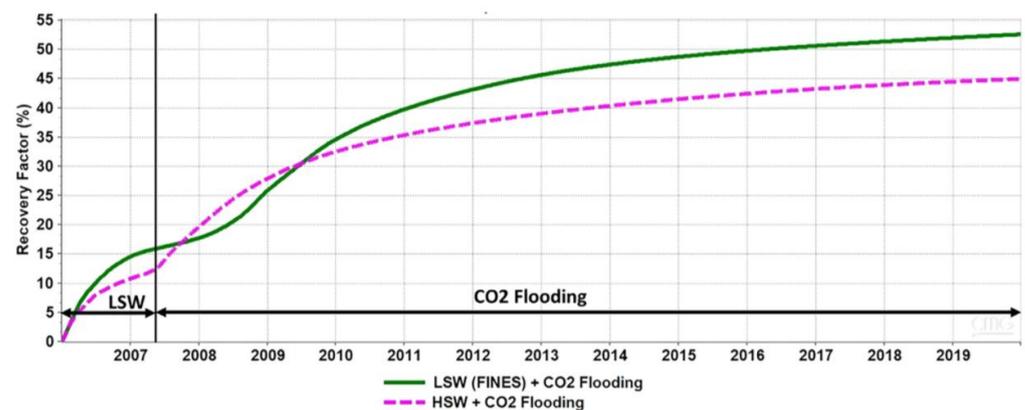


Figure 13. LSW + CO₂ flooding vs. HSW + CO₂ flooding at field scale [145].

Very limited simulation work has been performed with respect to CO₂ LSWAG injection in carbonate [110,149,150]. Al-Shalabi et al. [151] 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. [149] 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 [152], 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 CO₂ LSWAG injection, including CO₂ 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 CO₂ LSWAG injection. Therefore, investigating CO₂ LSWAG injection with hysteresis model, as well as history matching with experimental data could be considered for further research.

5.3. 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 14. Al-Abri et al. [97] 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. [9] 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. [91] for CO₂ LSWAG injection in carbonate reservoir. Chaturvedi et al. [8] and AlQuraishi et al. [96] 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. [7] 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. [95,98,153] as the mechanism. Moradpour et al. [99] 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.

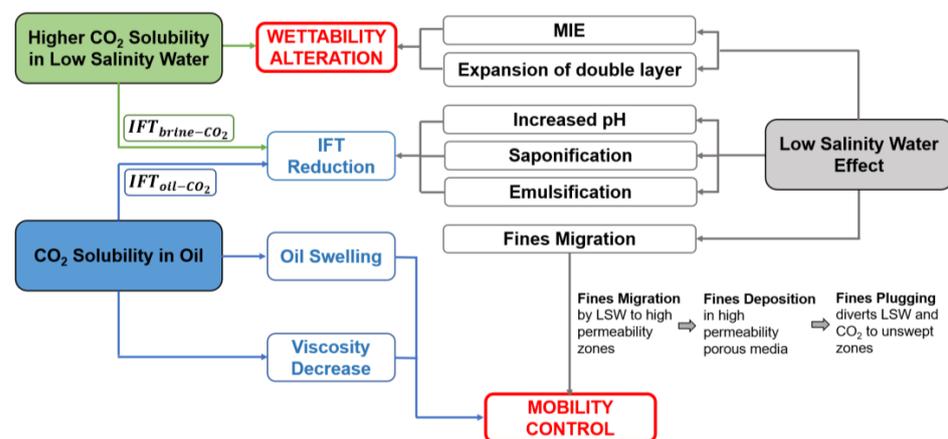


Figure 14. Proposed combined mechanisms of LSWI and CO₂ WAG injection in sandstone.

Based on the proposed mechanisms, wettability alteration and mobility control might be considered as the dominant mechanisms in CO₂ LSWAG injection. However, some investigations [10,11] 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 [6,145] 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 CO₂ LSWAG injection will yield the highest recovery.

5.4. Working Conditions and Screening Criteria for CO₂ LSWAG Injection

Based on the pervious core flooding experiments, the EOR potential of CO₂ LSWAG injection is not always shown (Table 9). 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 9, there is one case [7] 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 CO₂ LSWAG injection since there might be times that the dominant effect is either CO₂ or LSW. If the dominant effect is LSW, the presence of multivalent cations in formation brine should be added as one more requirement.

Table 9. Summary of CO₂ LSWAG injection EOR potential from core flooding experiments.

Potential for Enhanced Oil Recovery	Initial Wettability	
	Water-Wet	Intermediate-Wet to Oil-Wet
No Clay	1 reviewed article indicates EOR potential [7]	/
<0.5% Clay	2 reviewed articles indicate EOR potential [95,97] 2 reviewed articles indicate no EOR potential [11,96]	2 reviewed articles indicate EOR potential [9,98]
2–6% Clay	2 reviewed articles indicate EOR potential [8,96] 1 reviewed article indicates no EOR potential [10]	/

/: no experimental results found.

5.5. 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 [32]. 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 [151]. 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. [7] showed LSE in CO₂ LSWAG injection in samples that are kaolinite-free.

5.6. Environmental Aspects of CO₂

Commonly, sources of CO₂ for EOR operations are classified into three categories: (1) natural sources, indicating naturally occurring underground accumulations of CO₂ (purity is higher than 90%); (2) natural gas processing, where the produced gas contains significant amount of methane; (3) industrial processing, where CO₂ is captured from industrial plants [157]. Before the development of CCUS (carbon capture, utilization and storage) integration, natural sources of CO₂ are most-commonly used for oil enhancement. This brings about issues considering expenses and supply, as the long-distance transportation from the source site to the injection site is expensive and these CO₂ source reservoirs have a finite capacity and some are being depleted. With the development of CCUS hubs for carbon capture from emitting sources, the source for CO₂-assisted EOR is gradually switching from natural source to industrial processing, captured CO₂. This enables the oil and gas industry to address the global warming environmental issue and lower carbon emission.

6. Simulation Investigation on Hysteresis Effect

According to the research gap described in Section 5.5, investigation on the hysteresis effect during CO₂ LSWAG process is void. To fill this research gap, we have carried out simulation studies of hysteresis effect on miscible CO₂ LSWAG injection.

6.1. 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. [6] 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 [158]. The second approach is to use the three-phase hysteresis model developed by Larsen and Skauge [131] 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.

6.1.1. 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 [158,159] are founded on Land's trapping model [160]. 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

$$S_{gr} = S_{gcrit} + \frac{S_{g,max} - S_{gcrit}}{1 + C(S_{g,max} - S_{gcrit})} \quad (8)$$

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 Equation (9):

$$S_{gf} = S_{gcrit} + \frac{1}{2} \left[(S_g - S_{gr}) + \sqrt{(S_g - S_{gr})^2 + \frac{4}{C} (S_g - S_{gr})} \right] \quad (9)$$

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 15. 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 15), is computed with Equation (10):

$$K_{rg}^{imb}(S_g) = K_{rg}^{drain}(S_{gf}) \quad (10)$$

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.

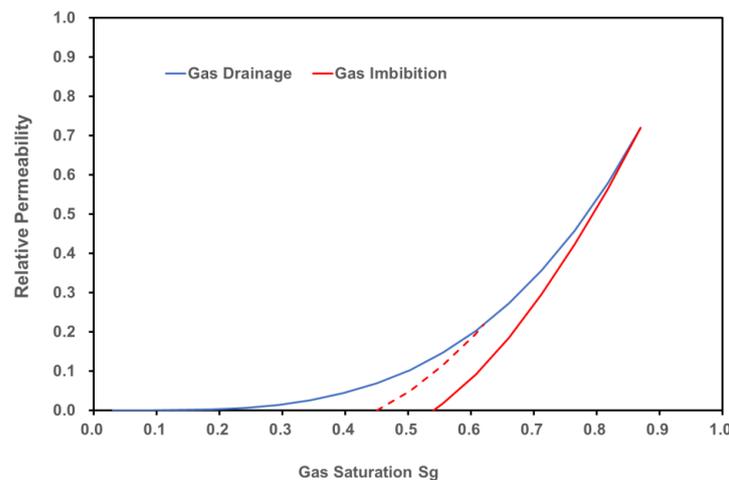


Figure 15. Carlson hysteresis model on the non-wetting gas phase.

The three-phase hysteresis model implemented in this study is based on the model from Larsen and Skauge [131]. 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:

$$K_{rg}^{drain} = \left[K_{rg}^{input} - K_{rg}^{input}(S_g^{start}) \right] \left[\frac{S_{wcon}}{S_w^{start}} \right]^\alpha + \left[K_{rg}^{imb}(S_g^{start}) \right] \quad (11)$$

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, [128]. Therefore, for an imbibition process with increasing water saturation, interpolation is

carried out between the two-phase and three-phase inputs (Figure 16) with Equation (12) to calculate the imbibition relative permeability (K_{rw}^{imb}):

$$K_{rw}^{imb} = K_{rw}^{W2} \left(1 - \frac{S_g^I}{S_{g,max}} \right) + K_{rw}^{W3} \left(\frac{S_g^I}{S_{g,max}} \right) \quad (12)$$

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.

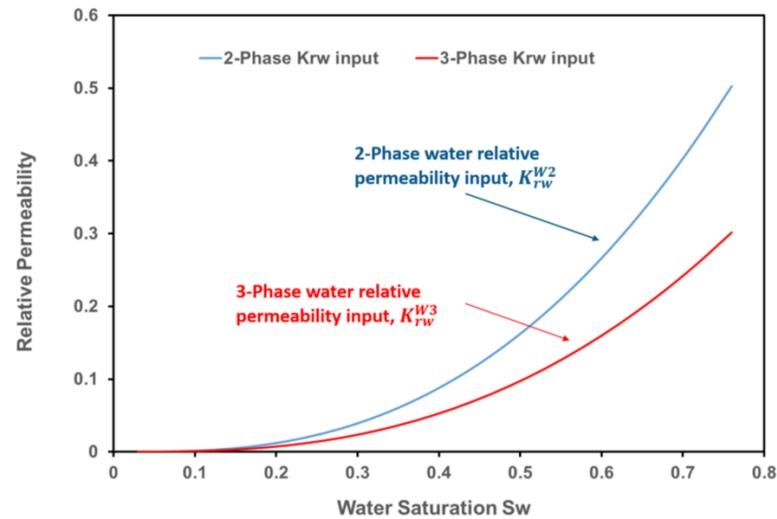


Figure 16. Phase and 3-Phase relative permeability input for the Larsen and Skauge model.

6.1.2. Core-Scale Model and LSWI Description

A composite core-scale model (Figure 17) with properties shown in Table 10 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 [4].

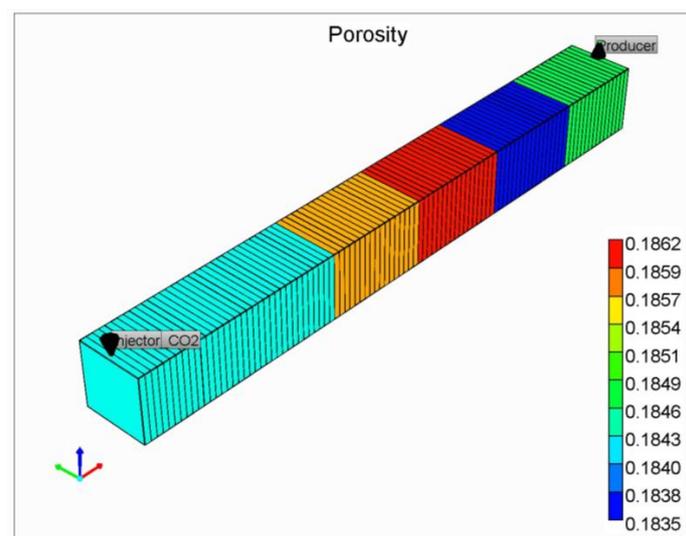
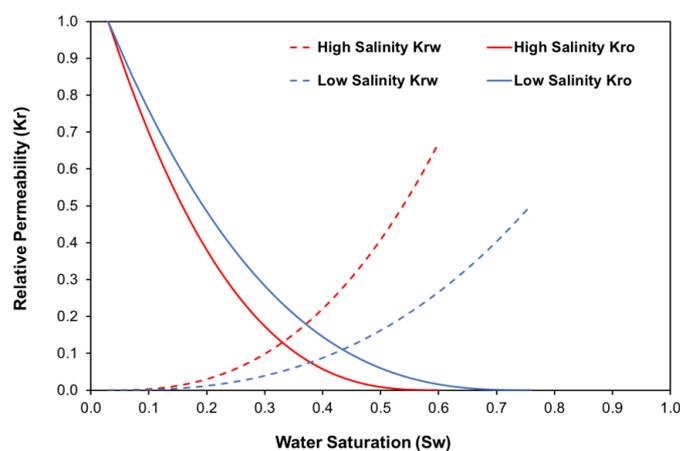


Figure 17. Composite core-scale model.

Table 10. Properties and operational parameters of the core-scale model.

Parameter	Value
Grid block system	100 × 1 × 1
Grid block sizes	$\Delta x = 0.312$ cm, $\Delta y = 3.345$ cm, $\Delta z = 3.345$ cm
Porosity	17 × 0.1845, 17 × 0.1845, 17 × 0.1859, 17 × 0.1862, 17 × 0.1835, 15 × 0.1846
Permeability (mD)	17 × 2412, 17 × 2235, 17 × 2280, 17 × 2285, 17 × 2180, 15 × 2240
Initial water saturation	0.03
Reservoir temperature	100 °C
Initial reservoir pressure	42,446 kPa (6156 psi)
Injection rate	11 cm ³ /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 m ³ /sm ³

Figure 18 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 11, 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 11. The salinity of the low salinity water is chosen to be 2000 ppm, which is within the salinity range for LSWI [58].

**Figure 18.** Relative permeability for high and low salinity water.**Table 11.** 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	1310	73
Ca ²⁺ , mg/L	3599	420	23
K ⁺ , mg/L	225	407	23
Cl ⁻ , mg/L	62,371	19,740	1104
SO ₄ ²⁻ , mg/L	233	2766	155
HCO ₃ ⁻ , mg/L	-	129	7
Total	102,430	35,746	2000

6.1.3. 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 [131]. 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. [135] and gas relative permeability reduction factor of 3.32 as suggested by Hosseini et al. [161]. The effect of salinity on three-phase hysteresis is also investigated with varying salinities (2000, 5000, 10,000, 20,000, 35,746 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.

6.2. 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.

6.2.1. Effect of Hysteresis Model on Oil Recovery

Table 12 summarizes the oil recovery factor with and without hysteresis for CO₂ LS WAG injection (2000 ppm low salinity water) and CO₂ WAG injection (35,746 ppm seawater). The two base cases are the CO₂ LS WAG and WAG injection with no hysteresis.

Table 12. Summary of simulation results.

Case	Recovery Scheme	Hysteresis Model	Land Parameter	Gas Reduction Factor	Recovery Factor	% Difference from Base Case
#1	CO ₂ WAG	None	N/A	N/A	85.4%	Base 1
#2		2 Phase	0.8	N/A	85.4%	0%
#3		3 Phase	0.8	3.32	85.7%	0.35%
#4	CO ₂ LS WAG	None	N/A	N/A	86.6%	Base 2
#5		2 Phase	0.8	N/A	86.1%	−0.8%
#6		3 Phase	0.8	3.32	86.1%	−0.8%

It is observed from Table 12 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 CO₂ WAG injection (#1 and #3), however, the opposite trend is observed for CO₂ LS WAG injection (#4 and #6). Comparing the differences of 2-Phase Carlson and 3-Phase Larsen and Skauge model in CO₂ 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 CO₂ 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 35,746 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.

6.2.2. Effect of Salinity

The effect of salinity is investigated through varying injection water salinities from 2000 ppm to 35,746 ppm (seawater) in the CO₂ WAG process (2000 ppm, 5000 ppm, 10,000 ppm, 20,000 ppm, and 35,746 ppm). Figure 19 shows the results with oil recoveries plotted against salinities.

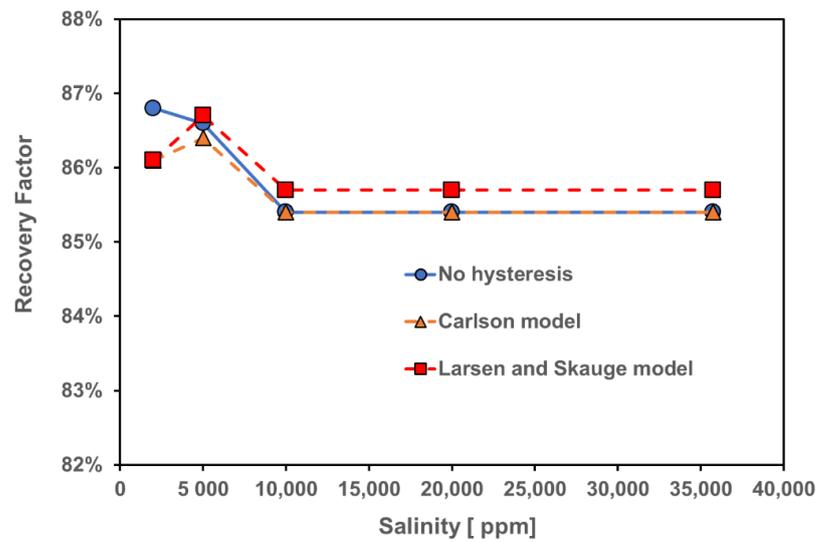


Figure 19. Oil recovery factor for CO₂ WAG injection hysteresis simulations with different salinities.

Even though changes in oil recovery with respect to salinity is relatively small in this core-scale simulation, the changing trend is worth mentioning since the effect might be magnified in the field scale. From Figure 19, oil recovery of CO₂ WAG injection with no hysteresis remains unchanged from 35,746 ppm to 10,000 ppm and increases with decreasing salinity from 10,000 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 10,000 ppm. Instead of a constant increase in oil recovery from 10,000 ppm to 2000 ppm, oil recovery slightly increases to a peak from 10,000 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 20 shows that oil recovery by only water injection increases from 100,000 ppm to 2000 ppm. Thus, the trend changing in oil recovery of CO₂ WAG injection might be mainly due to the hysteresis effect. CO₂ 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 20).

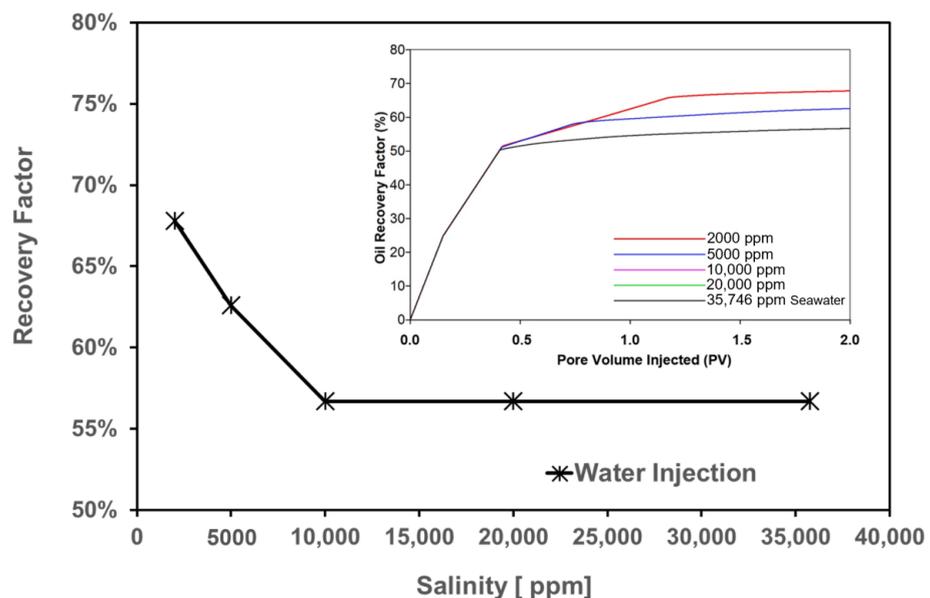


Figure 20. Oil recovery by water injection with varying salinities.

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.

7. Conclusions

This paper presents a review of the effect of different parameters on CO₂ LSWAG injection, and the independent and combined mechanisms of LSWI and CO₂ WAG injection. A simulation investigation on the hysteresis effect in CO₂ 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:

- 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;
- Laboratory experiments suggest that mobility control and wettability alteration (towards more water-wet) could be the dominant mechanisms for CO₂ LSWAG injection;
- Clay content might not be an essential requirement for EOR using CO₂ LSWAG injection as EOR potential has been observed with core samples with no clay content and core samples with less than 0.5% or 2–6% clay have reported both oil recovery increase or no oil recovery increase. This could be because the low salinity effect in a CO₂ LSWAG injection differs from LSWI alone. In a CO₂ LSWAG injection, low salinity effect could be similar to a LSWI, or similar to carbonated water injection as lower salinity leads to higher CO₂ solubility in water, resulting in in situ carbonated water effect for increased oil recovery.
- 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;
- 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 LSWAG 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;
- 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;
- 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
- Our simulation investigation on the hysteresis effect indicates that it is more accurate to include hysteresis in CO₂ LSWAG injection modeling and optimization. In our study with respect salinity effect on oil recovery considering hysteresis, higher oil recovery is obtained with salinity of 5000 ppm instead of 2000 ppm, indicating that lower salinity in a CO₂ LSWAG injection with hysteresis effect considered might not lead to higher oil recovery. 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.

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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 ₂ CO 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 ₂ SO 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
NPV	Net present value
OOIP	Original oil in place
ppm	Parts per million
PSO	Particle swarm optimization
PV	Pore volume
RSM	Response surface methodology
S _g	Gas saturation
S _{g,crit}	Critical gas saturation
S _{gf}	Free gas saturation
S _{g,max}	Maximum gas saturation at the flow reversal
S _{gr}	Trapped gas saturation
SO ₄ ²⁻	Sulfate ion
S _w	Water saturation
TDS	Total dissolved solids
UTCOMP	Compositional and multiphase flow simulator
WAG	Water-alternating-gas
WI	Wettability index
0NaCl	Without NaCl
0NaCl-d ₅ Ca	Without NaCl and 5-time diluted Ca ²⁺
0NaCl-d ₅ Mg	Without NaCl and 5-time diluted Mg ²⁺
0NaCl-d ₅ SO ₄	Without NaCl and 5-time diluted SO ₄ ²⁻
Variables and parameters	
M	Mobility ratio
V	Volume fraction
Greek letters	
ζ	Zeta potential
λ	Mobility
θ	Contact angle
β	Coefficient
v	Velocity

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