Mechanistic study of the carbonated smart water in carbonate reservoirs

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Abstract: Carbonated smart water (CSMW) injection has drawn considerable interest, especially in the last decade. This interest stems from its results in the recovery factor enhancement and the storage of carbon dioxide. This method has been mainly studied for sandstone formations, and less devotion has been given to carbonates, especially in naturally fractured reservoirs. This paper examines the effect of the CSMW on the recovery factor in carbonate homogenous and fractured reservoirs and investigates the most effective mechanisms. Furthermore, the capability of the CSMW to store the CO₂ in the reservoir has been tested. This work has been established based on core flooding experimental data, using a compositional simulator, and extending the core results to a pilot model. The composition and salinity values of the CSMW have been specified using optimization and sensitivity analysis tools. Geochemical reactions and CO₂ solubility in the CSMW have been simulated using the PHREEQC. In the core scale, the CSMW showed 14, 7.6, 26.8% more oil recovery than Smart Water (SMW), Carbonated Seawater (CSW), and Seawater (SW), respectively. In the pilot model, CSMW recovered more oil than the SMW by 5–8% based on the heterogeneity and fracture availability. Viscosity reduction is one of the main mechanisms behind the oil recovery increment. More than 30% of viscosity reduction was observed for all studied cases. Ions exchange and mineral dissolution processes were also pivotal. A higher recovery has been obtained in the fractured reservoir after the breakthrough due to the CO₂ diffusion from the fractures into the matrices and the spontaneous imbibition process, where those mechanisms need a long time to act effectively. More than 50% of the injected CO₂ within the CSMW has been captured in the reservoir’s residual oil and water. It has been concluded that the stored CO₂ in the reservoir depends on the amount of residual oil saturation, where the higher the remaining oil in the reservoir, the higher the stored CO₂ amount. © 2021 The Authors. Greenhouse Gases: Science and Technology published by Society of Chemical Industry and John Wiley & Sons Ltd.

Keywords: enhanced oil recovery; carbonated smart water; fractured reservoir; CO₂ storage; CO₂ retention

Introduction

Carbonate reservoirs represent more than two-thirds of oil and gas reserves globally, while sandstones and other lithologies acquire the remaining reservoirs.¹ As it is well known, CO₂ is one of the most potent greenhouse gases emitted, contributing up to 72–77% in greenhouse gases.² Because of the harmful effect of this gas on the environment, disposal of this gas was indispensable. One of the best ways to dispose of CO₂ is to store it underground. The cooptimization methods are very efficient methods to take advantage of this CO₂ gas to enhance the oil recovery (EOR) and store the CO₂ in...
the formation.3–5 One of those co-optimization methods is carbonated water (CW) injection, where the injected water is enriched with CO₂ at the surface and injected as one fluid. However, CW injection proved significant in the enhancement of the oil recovery and typical decrease in the residual oil saturation over the traditional seawater injection.6–8

In 1958 ORCO (Oil recovery cooperation) performed the first commercial implementation of carbonated water flooding in the Dewey-Bartlesville Field, Washington County, Northeast Oklahoma, the K&S project.9 However, limited studies and field applications have been reported for more than three decades. Recently more interest has been shown in the process with the objective of EOR and CO₂ storage.10 DuetotherecentLowSalinityWaterflood(LSW)method, the original carbonated water can take advantage of the LSW mechanism, especially if the low water salinity composition is optimized.

The limited published studies regarding carbonate water in carbonate reservoirs are mainly related to experimental and modeling core data, where the fractures are not considered.5 Besides, the low salinity water used in the previous studies are based on the dilution of formation or sea water. Therefore, further studies are required to examine the fracture effect and related mechanisms on the process’ overall performance and the low salinity water composition. This work aims to study carbonated smart water’s effects on carbonate rocks and fractured reservoirs concerning oil recovery improvement and CO₂ storage capacity. Also, the carbonated water composition is optimized for maximum recovery instead of the conventional low salinity water.

In the following sections, the state of the art of the carbonated low salinity water flooding and the storage capacity of CO₂ is provided with emphases on the postulated mechanisms and modeling.

Carbonated low salinity water flooding

Carbonated low salinity water (CLSW) is a combination of low salinity water and CO₂ (supercritical), coexisting in the same phase at p > 1072 psi and T > 87.8°F.10,11 CLSW takes advantage of the high CO₂ solubility in the low salinity water (salting-in phenomenon), which ensures a high mass transfer of CO₂ from the CW to the oil, based on 3–7 times higher affinity of CO₂ to be dissolved in oil than in water.3–5 CW had an enhanced sweep efficiency compared to the other CO₂-EOR methods such as CO₂ injection and water-alternating-gas (WAG) due to oil viscosity reduction and CW’s ability to overcome the shielding effect.6,12 The shielding prevents the CO₂ (free phase) from being in contact with the oil, but in the carbonated water, the CO₂ is dissolved in the water as an aqueous phase.3,13–15

When the CO₂ enriched water is in contact with the oil, the CO₂ will diffuse from the aqueous phase to the oil phase, leading to an oil swelling, thus decreasing the oil viscosity, enhancing the ultimate recovery. This diffusivity is controlled by the CO₂-brine diffusion coefficient, which is a function of temperature, salinity, porosity, tortuosity, salt composition, and pressure (small effect). The diffusion coefficient of CO₂ in pure water is 1.86 ± 0.26 × 10⁻⁹ m² s⁻¹ over the range of pressures (5–50 bar) tested at 26 °C.16 This coefficient decreases as a power-law correlation at a 5 M salinity value of NaCl to become one-third of the pure water at the same temperature.6,17 In this case, time is the most important factor. The more prolonged the connection between the CO₂ and oil, the higher the diffusion efficiency. Hence, the recovery will increase because of the mobilization of the residual oil ganglia. The partition of the CO₂ between the oil and water can be described using the partition coefficient of CO₂ (Eqn 1).

\[
k_{CO_2,OW} = \frac{C_{CO_2,O}}{C_{CO_2,w}}
\]

where \( k_{CO_2,OW} \) denotes the oil-water partition coefficient of CO₂; \( C_{CO_2,O} \) is the concentration of CO₂ in the oil phase, and \( C_{CO_2,w} \) represents CO₂ concentration in the CW phase.6

The solubility of carbon dioxide in brine at a constant salinity increases with pressure increase and temperature decrease.13 Water salinity directly relates to the CO₂ solubility, where the lower the water salinity, the higher the solubility of CO₂ due to the salting-in phenomenon. Moreover, the composition of the salt has an important effect on the volume of the dissolved CO₂ at the same level of salt ionic strength (mol kg⁻¹), where the salts influence the magnitude of CO₂ solubility in the following order: KCl < CaCl₂ < MgCl₂ < NaCl < Na₂SO₄.6

Water composition, CO₂ fraction in the water, oil density and viscosity, reservoir pressure and temperature, and the implementation stage are the most important factors that have to be considered when CLSW is applied. The recovery factor of the
CLSW injection is higher when used as a secondary stage and less when used as a tertiary or quaternary stage. The reason is that, in the tertiary stage, the injected CLSW will flow in the previously flooded water pathways. Consequently, it will contact the flooded pores (regions) only, which is not the case in the secondary stage. On the other hand, oil swelling is more effective due to the larger mass of the transferred CO₂. In the secondary flooding, a long contact time between the CLSW and oil is available, and the contact starts from the beginning of flooding.\(^3\),\(^13\),\(^10\),\(^4\),\(^18\),\(^8\)

**CO₂ storage (sequestration)**

Storing CO₂ in the conventional methods included either storing in underground geological traps (one target) or by injecting a pure CO₂ to enhance oil recovery and sequestrate CO₂ (dual-target) as per the EOR method. Those methods may encounter some complications and flaws, such as low sweep efficiency.\(^3\),\(^19\) Based on the conducted laboratory experiments and the simulation models, CO₂ storage in the formation as CO₂-enriched water and/or dissolved in the residual oil was a secure and beneficial application for the environment and oil recovery.\(^6\) Moreover, this technique requires a significantly lower pressure system and CO₂ amount than used in the pure CO₂ injection method.\(^20\)

In the CLSW injection, some experiments showed that up to 17–45% CO₂ volume was captured in the formation due to the salting-in phenomenon.\(^5\) When the CO₂ is dissolved in the water, water will have lower mobility due to the higher viscosity. Therefore, the stored CO₂ in the remaining water will eliminate the risk of buoyancy-driven leakage, thus securing storage.\(^20\) The exsolved CO₂, in turn, has low mobility due to the dispersed morphology of its bubbles in the pore space; therefore, CO₂ will remain in the reservoir a long time after oil production. Furthermore, the remaining oil will have a considerable amount of CO₂, which will still be stored in the reservoir.\(^21\)

The fraction of the stored CO₂ differs based on which stage of recovery the CLSW injection is applied. Bakhshi et al.\(^3\) and Mosavat and Torabi\(^22\) found out that the stored CO₂ was 61% in the tertiary mode, while it was 40.7% in the secondary scenario, due to more amount of residual oil that could sequestrate CO₂. This conclusion did not match what Shakiba et al.\(^18\) reported in the experimental investigation, where the TCW and SCW captured the same amount of CO₂ with similar physical properties.

The amount of storable CO₂ in the reservoir can be estimated using Eqn 2. This equation uses the amount of injected CO₂ instead of the total capacity of CO₂ in the reservoir\(^3\):

$$\text{CO}_2 \text{ Retention} = \frac{M'_{CO_2} - M''_{CO_2}}{M'_{CO_2}} = \frac{M''_{CO_2}}{M''_{CO_2}} (2)$$

where \(M'_{CO_2}, M''_{CO_2}\), and \(M''_{CO_2}\) are, respectively, the mass of CO₂ injected in, produced from, and stored in a reservoir.

**Simulation investigations of carbonated water injection**

One of the first CW models has been developed by De Nevers\(^23\) based on the Buckley–Leverett type linear flow model to predict the CW performance. The capillary and gravity forces were ignored in the model; however, the effects of oil viscosity reduction and oil swelling due to the CO₂ dissolution were considered. They concluded that the viscosity reduction is the main mechanism of the oil recovery enhancement, and oil swelling contributes to a lower extent. Ramesh and Dixon\(^24\) developed a 2-D dynamic three-phase flow mathematical model, including the solubility of CO₂ in oil. They used the implicit method for pressure equation discretization. CW modeling was later extended to a compositional simulator by Mansoori\(^25\) to identify the effect of the solubility of CO₂ in the water on oil recovery by CO₂ flooding. Based on the Soave–Redlich–Kwong (SRK) equation of state, the phase equilibrium and CO₂ solubility in water were calculated. This model was developed to simulate 1-D and 2-D displacement processes, and Newton’s method was used to discretize and solve sets of equations until convergence was achieved. In this model, the water and CO₂ were separately injected, and it was suggested that CO₂ be dissolved into the water during injection and into the reservoir in different proportions. They concluded that the higher the CO₂ solubility in water, the higher the recovery factor.

Chang et al.\(^26\) presented a 3-D, three-phase compositional model to simulate CO₂ flooding, including CO₂ solubility in water, where gravity and capillary terms were also included. Fully implicit and IMPES formulations were included in the model, and a cubic equation of state was utilized to model the oil- and gas-phase densities and fugacities. In this model, the CO₂ was dissolved into water in an aqueous phase before the injection.
Kechut et al.\textsuperscript{10} conducted a series of carbonated water flood experiments and used Eclipse 300 (E300) simulator to simulate those experiments. They injected the water and the CO$_2$ separately in two wells, and the model included another well as a producer. The model assumed homogenous porosity and permeability, and capillary pressure was considered to be zero. Some simulators included the thermodynamic equilibrium (such as CMG), and some did not (such as the UTCOMP). UTCOMP simulator was recently developed by the University of Texas at Austin (Sanaei et al., 2019). Lee et al.\textsuperscript{5} used GEM software developed by CMG to model LSW core flooding experiments. GEM simulator considers the geochemical reactions and multi-ion exchange (MIE) theory. The PHREEQC simulator is used to calculate the solubility of CO$_2$ in the salinity water, the reservoir pressure, and temperature conditions.

**Theoretical analysis of potential CSMW mechanisms**

Measurements, such as interfacial tension (IFT), contact angle, nuclear magnetic resonance (NMR), and zeta $\zeta$-potential, have been conducted to study the recovery mechanisms of the carbonated water process. Besides, imbibition and core flooding tests have been conducted to determine the responsible mechanisms for the high recovery of the CLSW process. The proposed mechanisms for the obtained high recovery can be summarized as follows:\textsuperscript{3,27} (Luo et al., 2018)\textsuperscript{28,13,20,4,5,29,7,30}:

1. Mineral dissolution due to the reaction between the CW and the reservoir rocks.
2. The solubility of the CO$_2$ into oil can trigger the liberation of light components in the form of a new gaseous phase, which results in a reduction of the oil viscosity (the main recovery mechanism in the heavy oil).
3. Fluid redistribution.
4. Alteration of the water/oil contact angle, which is a direct indicator of wettability alteration of the crude oil/water/rock system (wettability alteration toward more water-wet).
5. Swelling of oil due to CO$_2$ diffusion results in a coalescence of the isolated oil ganglia,\textsuperscript{27} thus enhancement of the macroscopic sweep efficiency (the main mechanism in the light oil).
6. Ions exchange.
7. Increase the viscous force of the injecting fluid.

**Multi-ion exchange**

MIE is considered in many studies to be the main mechanism of the low salinity water flooding as an EOR method. The mechanism behind this importance is the wettability alteration of the oil-wet or mixed-wet reservoir rocks toward water-wet, allowing a release of the adsorbed electrically polar oil components (e.g., carboxylic oil component) from the rock surface. This mechanism occurs by replacing the rock surface’s cations with the divalent ions from the injected low salinity water, thus changing the rock’s surface charge. In other words, MIE in carbonates is a process of reactions of surface potential determining ions (PDIs), where SO$_4^{2-}$ will adsorb on the positive rock surface, attracting the positive divalent ions (Mg$^{2+}$, Ca$^{2+}$). This adsorption of SO$_4^{2-}$ will affect the system in two ways:

First of all, sulfate services as a catalyst; therefore, a coadsorption of Ca$^{2+}$ and/or Mg$^{2+}$ will happen on the stern layer of SO$_4^{2-}$ due to the reduction of the electrostatic repulsive force (positive ions and the positive rock surface), forming an electrical double layer on the carbonate rock surface. Then, it will release the negative carboxylic oil component. This is because the negatively charged sulfate ion is relatively strongly attracted to the carbonate rock surface compared to the carboxylic acids rendering the rock surface less oil-wet and allowing the oil to flow through the pore throats\textsuperscript{4,31,32}

**Mineral dissolution**

The generated carbonic acid in the CW can dissolve carbonate minerals. An increase of the porosity by 16.15\% was reported when the CW was injected into the carbonate cores, but no appreciable permeability change was noticed.\textsuperscript{6} In contrast, Perez et al.\textsuperscript{33} reported an increase of 20.33\% over the initial permeability. However, for some samples, pores with relatively small diameters disappeared when CW was used.\textsuperscript{34} The increase in pore volume due to calcite dissolution is calculated using Eqn 3:\textsuperscript{34}

\[
V_{\text{pore}} = \frac{m_{\text{Calcite}}}{\rho_G}.
\]  

where $V_{\text{pore}}$, $m_{\text{Calcite}}$, and $\rho_G$ are the increase in pore volume (cm$^3$), the dissolved calcite mass (g), and calcite density (g cm$^{-3}$), respectively. The calcite dissolution and precipitation rate is related to the mineral reaction, which is handled in the equilibrium reactions.\textsuperscript{5} The dissolution (if occurs) will result in a larger pores diameter, thus lower capillary pressure in
those pores, which could enhance the microscopic sweep efficiency. Kilybay et al. reported some noticeable PSD changes based on the cores' NMR studies. This change occurs in the micro and macro scale, where they noticed a reduction in the micropores refers to blockages of porosity due to deposition of sulfate scales or produced fines. The observed increase in the macro-pores can refer to the carbonate dissolution (mainly Ca\(^{2+}\) and Mg\(^{2+}\)). The overall measured porosity in the experiments indicated an increase in the porosity, which can be explained by the higher volume of the dissolved minerals than the precipitated in the small pores.

The studied rock’s heterogeneity has an important effect on mineral dissolution, as Nunez et al. concluded. They reported that the mineral dissolution increases in the higher porosity region and decreases in the lower one. This can be clarified based on the interstitial velocity variation. The carbonated water flow presented lower interstitial velocity in the high porosity area, providing a longer time for the CW to contact the minerals, increasing the dissolution rate. The opposite happened in lower porosity regions. This conclusion has also been observed in Kilybay et al. experimental results in the PSD curves and NMR plots. The higher the permeability, the more the dissolved minerals, especially in the macroporosity region.

Wettability alteration

Yousef et al. observed a change in the contact-angle measurements in the core flooding experiments of carbonate rocks when they changed the ionic composition and the injected water’s salinity. They found out that this change significantly impacted the rock wettability (to a more water-wet system) due to the IFT reduction. Carbonated water reduces the IFT leading to an increase in capillary number (Nc) by orders of magnitude enhancing, in turn, the oil recovery significantly. Ruidiaz et al. reported that the wettability alteration is independent of the brine concentration and the presence of CO\(_2\) in the water. They concluded that the CO\(_2\) or its derived ions might prevent the wettability alteration mechanism. The dissolved CO\(_2\) tends to move to the surface (oil-water interface) due to the low reactivity toward polar water molecules. When CO\(_2\) molecules reach the surface, they will decrease the available space for water molecules, imposing some spatial (conformational) constraints onto water molecules. In response, IFT is reduced as a result of the weakened hydrogen bonds among water molecules. Consequently, IFT in the CW-oil interface is less than it in the brine-oil system. Hamouda and Bagalkot reported the same observation when they used carbonated water with MgCl\(_2\). This could be attributed to the reduction of interfacial tension and higher hydration energy of Mg\(^{2+}\). Hence, a tight bond to the first hydration shell \([\text{Mg(H}_2\text{O)}_6]^{2+}\) might be generated. Consequently, this increases the effective size at the interface and diminishes the IFT.

Oil swelling

When the carbonated low salinity water (CLSW) is injected, the oil will swell due to the CO\(_2\) diffusion from the water into the oil. Perez et al. reported that oil swelling and CO\(_2\) solubility increase by increasing the pressure, diminishing the temperature, and lower water salinity. Zhao et al. reported that the behavior of the dissolved CO\(_2\) in the oil has two different regions. In the first region, when the temperature increases, the CO\(_2\) solubility decreases, leading to a lower oil swelling. Reversely in the second region, the CO\(_2\) solubility increases when the temperature increases at a given pressure.

Methodology

This work has been conducted based on core flooding experimental data to validate the generated model using history matching. Upon building the model optimization and sensitivity analysis studies were conducted using CMG simulator. The objective is to determine the optimum water composition (smart water) that gives the highest recovery in the carbonated water flooding. The GEM simulator was used to generate carbonated smart water allowing the CO\(_2\) to be injected in one phase with the injected water (aqueous phase). PHREEQC simulator was used to calculate the molality of the dissolved CO\(_2\) in water. The carbonated water was then assigned as the injected water in the injector. The results were compared with the diluted Seawater. The obtained optimized water was expanded to four pilot cases, namely, nonfractured homogenous reservoir, Nonfractured heterogenous reservoir, fractured homogenous reservoir, and fractured heterogenous reservoir. The stepwise methodology is summarized in Fig. 1.
Table 1. Experimental data

|            | Core properties | Oil properties | Water properties | Results |
|------------|-----------------|----------------|-----------------|--------|
| **D (cm)** | 3.785           |                |                 |        |
| **L (cm)** | 14.48           |                |                 |        |
| **PV (cm³)** | 15.6            |                |                 |        |
| **K (mD)**  | 0.901           |                |                 |        |
| **φ**      | 0.096           |                |                 |        |
| **API°**   | 33.8            | 0.8277         | 0.4168          |        |
| **Density (g cm⁻³)** |            |                |                 |        |
| **μ (cp)** | 140             | 2000          |                 |        |
| **T (°F)** |                |                |                 |        |
| **p (psi)** |                |                |                 |        |
| **NaCl (ppm)** | 40 000        | 0.000144   | 0.63            |        |
| **Inj-rate (m³/d)** |            |                |                 |        |
| **μ (cp)** |                |                |                 |        |
| **Used-water RF %** |            |                |                 |        |
| **Inj-PV** |                |                |                 |        |

| Used-water | NaCl-Water | 35 | 2.5 |
| Carbonate-NaCl Water | 53 | 3.7 |

Overview of the related experiment

This work has been established based on the core-flooding experimental data shown in Table 1. In the experimental work, the effects of the carbonated water injection were studied by injecting 2.5 pore volume (PV) water with a salinity of 40 000 ppm of NaCl. Subsequently, the process was repeated by injecting 3.7 PV carbonated NaCl-water at the same salinity. The carbonated water caused an oil recovery increment by 13.6% more than the conventional water flooding and a 50.6% CO₂ storage from the total injected volume. The injected water was fully saturated with the CO₂ (0.983 mol kg⁻¹ water) at 2000 psi and 140 °F. The mineral dissolution, porosity changes, ion exchange, and viscosity reduction, which was thoroughly investigated in experimental work, will be considered in this simulation work. The core, water, oil properties, and the experiment results are given in Table 1.

Model Development

Core model

A 1-D core-flooding model was constructed to represent the data of the carbonated water flooding experiment. A 100 × 1 × 1 cartesian grids model in the x, y, and z directions was used to overcome the numerical dispersion that appeared in the less-grids model. No considerable change was observed when the number of cells was increased by more than 100 cells. The reservoir pressure and temperature, and oil components used to generate the PVT model are given in Table 2.

The PVT model was imported into the generated core model. Peng–Robinson equation was chosen to represent the model of equation of state. The core position was supposed to be 10 m above the oil-water contact to ensure that no external water influx contributed to the production results. No external
forces affected the processes. Based on the experimental core data, 95% calcite and 5% dolomite rock model were used as an oil-wet carbonate reservoir to study the geochemical reactions, mineral dissolution, ion exchanges, wettability alteration, and viscosity reduction when the carbonated water is injected. A constant water injection rate was assigned in the injector (core inlet), and constant bottom hole pressure was applied in the producer (core outlet). A geochemical reactions [Eqn 4–20] model was implemented based on the database of the PHREEQC simulator. The following general chemical reactions have been used based on the mineralogy of the rocks:

Geochemical reactions:

\[
\begin{align*}
H^+ + OH^- & \leftrightarrow H_2O \\
CO_2 (aq) + H_2O & \leftrightarrow H^+ + HCO_3^- \\
H^+ + CaCO_3 & \leftrightarrow Ca^{2+} + HCO_3^- \\
H^+ + MgCO_3 & \leftrightarrow Mg^{2+} + HCO_3^- \\
H^+ + NaCO_3^- & \leftrightarrow Na^+ + HCO_3^- \\
CaHCO_3^- & \leftrightarrow Ca^{2+} + HCO_3^- \\
MgHCO_3^- & \leftrightarrow Mg^{2+} + HCO_3^- \\
NaCO_3^- & \leftrightarrow Na^+ + HCO_3^- \\
H^+ + MgOH^+ & \leftrightarrow H_2O + Mg^{2+}
\end{align*}
\]

(4) – (12)

Mineral dissolution/precipitation:

\[
\begin{align*}
CaHCO_3^- + H^+ & \leftrightarrow Ca^{2+} + HCO_3^- \\
Dolomite + 2(H^+) & \leftrightarrow Ca^{2+} + 2(HCO_3^-) + Mg^{2+}
\end{align*}
\]

(19) – (20)

The adopted model of the reaction between species in the aqueous phase has the following stoichiometry in Eqn 21:

\[
\sum_{k=1}^{n_{aq}} v_{ka}^a A_k = 0, \ a = 1, \ldots , R_{aq}
\]

(21)

and \( n_{aq} = n_c + n_a \), where \( n_{aq} \) refers to the number of components in the aqueous phase, \( n_c \) the gaseous components that are soluble in the aqueous phase, \( n_a \) components that exist only in the aqueous phase. \( a \) indicates the aqueous reaction, \( v_{ka} \) the stoichiometry coefficients, \( A_k \) is the chemical symbol for the \( k \)th aqueous species, and \( R_{aq} \) is the number of reactions between aqueous components (Eq. 22).

\[
H^+ + HCO_3^- - CO_2 (aq) - H_2O = 0
\]

(22)

Whereas the mineral dissolution/precipitation chemical reaction has the following stoichiometry (Eqn 23):

\[
\sum_{k=1}^{n_m} v_{kp}^\beta A_k = 0, \ \beta = 1, \ldots , R_{mn}
\]

(23)

Where, \( n_m \) is the total number of components (minerals and aqueous), \( R_{mn} \) is the number of reactions between minerals and aqueous components (Eqn 24 and 25)

\[
Ca^{2+} + CO_3^- - \text{Calcite} = 0
\]

(24)
Dissolution/precipitation equation as follows:

\[ \ln \sum_{k=1}^{n_{aq}} v_{\text{aq}}^a A_k = 0, \ a = 1, \ldots, R_{aq} \]  

(25)

Chemical-equilibrium reactions are modeled with the chemical equilibrium constant \( k_{eq,a} \) for the aqueous reaction \( a \), as the following equation (Eqn 26):

\[ Q_a - K_{eq,a} = 0, \ a = 1, \ldots, R_{aq} \]  

(26)

with \( Q_a = \prod_{k=1}^{n_{aq}} a_k^v_k \)

where \( Q_a \) is the activity product, \( a_k \) is the activity of component \( k \), and \( v_k \) are the stoichiometry coefficients.

It is worth noting here that \( K_{eq,a} \) values could be obtained from specific tables as a function of temperature for many aqueous reactions. The activity \( a_i \) is a function of the activity coefficient \( \gamma_i \) and molality \( m_i \) (moles per kg of \( \text{H}_2\text{O} \)) as follows (Eqn 27):

\[ a_i = \gamma_i m_i, \ i = 1, \ldots, n_{aq} \]  

(27)

Ionic activity coefficients in the CMG are modeled for the nonideal solutions (most cases) using the B-dot model (Eqn 28):

\[ \log \gamma_i = \frac{A_y Z_i^2 \sqrt{I}}{1 + c_{a_i} B_y \sqrt{I}} + \dot{B}I \]  

(28)

where \( A_y, B_y, \) and \( \dot{B} \) are temperature-dependent parameters, \( c_{a_i} \) is the ion size parameter. \( I \) is the ionic strength given by (Eqn 29):

\[ I = \frac{1}{2} \sum_{k=1}^{n_{aq}} m_k Z_k^2 \]  

(29)

where \( Z_k \) is the charge of the \( k \) ion.

On the other hand, the rate-dependent reactions are modeled using the rate law for the mineral dissolution/precipitation reaction equation as follows:

\[ r_\beta = A_\beta k_\beta \left( 1 - \frac{Q_\beta}{K_{eq,\beta}} \right), \ \beta = 1, \ldots, R_{mn} \]  

(30)

where \( r_\beta \) is the rate, \( A_\beta \) is the reactive surface area for mineral \( \beta \), \( k_\beta \) is the rate constant of mineral reaction \( \beta \), \( K_{eq,\beta} \) is the chemical equilibrium constant for mineral reaction \( \beta \), and \( Q_\beta \) is the activity product of mineral reaction \( \beta \).

After implementing the geochemical reactions and the PVT model, core flooding was simulated using the GEM. In the first case, the composition of the brine and the injected water was 40,000 ppm NaCl-water. About 2.3 PV water was injected, and the recovery factor was obtained. 3.5 PV carbonated NaCl-water with the same salinity was then injected in a separate model. The relative permeability curves related to those in the water experiment were obtained based on the generated models and history matching results. The generated relative permeability curves are implemented for the next step of modeling and simulation. In the carbonated water case, the simulation case showed slightly more ultimate oil recovery due to the GEM assumption, which is the instantaneous equilibrium state of \( \text{CO}_2 \). Due to this instantaneous equilibrium and complete mixing, the commercial simulators usually overestimate the RF values for CWI processes. 6

The next step in this methodology is studying the effect of different divalent ion concentrations on the recovery obtained from the core flooding data. Among the trials, sulfate ion has been found to have the maximum effect on oil recovery. As can be seen from Fig. 2, oil recovery has been improved by 10% when 50 ppm sulfate is added to the base case (40 000 NaCl carbonate water). Hence water composition variation, especially the divalent ions, is considered for the smart water optimization to be used in the pilot scale.

### Smart water injection (SMW)

The purpose of this section is to find out the optimum water composition, which maximizes oil recovery. Seawater (SW) has been used in waterflooding and low salinity water injection in the fields; it is used as the base case for further study. Then, this water will be saturated with \( \text{CO}_2 \) as carbonated smart water. The optimized smart water will be used in the next part to study the pilot. The used formation and injection waters (Seawater) in this part of the study are published by Lee et al.5 with salinity values of 26 958 ppm and 36 809 ppm (Table 3), respectively. Based on the core flooding results, \( \text{SO}_4^{2-} \) is selected as the main studied component.
Two approaches are considered for optimization, namely, advanced statistical analysis and traditional dilution. The CMOST intelligent and analysis optimization tool available in the CMG is used for optimization. Figure 3 illustrates a block diagram of the two methods and the related optimization approach.

The 36 809-ppm seawater is assigned in the injector, and water composition is optimized by using CMOST optimization analysis tool. The concentrations of each component are changed in the simulator randomly, and several results are obtained. The results indicated an optimum case with almost 5000 ppm, which gave the highest recovery in the studied range (2000–50 000 ppm); still, it cannot be considered as the final optimum solution due to the random distribution of the water ions concentrations. Therefore, the Morris and Sobol analysis optimization was used to define and evaluate the most effective ions on the recovery factor in the 2000–6000 ppm range. From those analyses, $\text{SO}_4^{2-}$ was found to be the most influential parameter in this study, as was observed by Al-Attar et al.\textsuperscript{43} and Zhang et al.\textsuperscript{44} The $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ were found to have a less significant effect. The sensitivity analysis results in the range of 2000 to 6000 ppm were compared, and the optimum value of each ion was chosen to form the smart water composition. The optimum salinity was found to be 3963.3 ppm, as represented in Table 3.

Moreover, 10 times diluted seawater (0.1 SW) was also studied (Table 3). The results were compared with the obtained smart water, which proved that the low salinity water represented as the diluted water cannot always be used as smart water.

The designed smart water was fully saturated with $\text{CO}_2$ to configure the carbonated smart water. $\text{CO}_2$ saturation value, under the experiment $p$ and $T$ conditions, was identified by the PHREEQC simulator (1.13 mol kg\textsuperscript{-1} water) and has been included in the GEM model. The smart water capacity to dissolve the $\text{CO}_2$ is more than the high salinity water (0.983 mol kg\textsuperscript{-1} water) due to the salting-in phenomena. The $\text{CO}_2$-saturated smart water or the carbonated smart water (CSMW) was injected into the carbonate core, and the results were compared to the SMW injection case.

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Table 4. Pilot properties.

| Direction | I  | J  | K  |
|-----------|----|----|----|
| Distance (M) | 275 | 275 | 6  |
| Cells      | 11 | 11 | 2  |
| Matrix-porosity | 10% | 10% | 10% |
| Fracture-porosity | 1%  | 1%  | 1%  |
| Matrix-permeability (mD) | 0.901 | 0.901 | 0.901 |
| Fracture-permeability (mD) | 1000 | 1000 | 500 |

Pilot-scale model

The model was expanded to a (300 × 300 × 6 m) 3D, two-layer pilot model, as shown in Table 4 and Fig. 5. One injection well and four production wells were designed in the model, where the same porosity and permeability, as in the core scale model, were assigned in the first model. An injection rate of 15 m$^3$ day$^{-1}$ was assigned in the injector, and the same bottom hole pressure was applied in producers, as in the outlet of the core. The obtained CSMW was injected into the pilot. To study the effect of reservoir heterogeneity on the recovery factor, the porosity, and subsequently, the permeability was randomly distributed in each layer of the second model, as shown in Figs. 4 and 5. The same CSMW was used in the models.

In the last case, fractures were included in the homogenous and heterogenous models. The effects of the CSMW on the minerals, fractures, matrix, and the RF were analyzed and compared with SMW cases. New relative permeability curves for the fractures were included in the prior non-fractured model, and a dual porosity- dual permeability model was implemented to represent the fracture system. The relative permeability curve of the fractures was included as straight lines with 45°.

Results and discussion

The effects of matrix heterogeneity and fractures for the studied cases, namely, homogenous nonfractured, homogenous fractured, heterogenous nonfractured, and heterogenous fractured systems, are discussed. The
effect of different mechanisms such as ion exchange, mineral dissolution, viscosity reduction, and wettability alteration will also be considered in detail.

Recovery factor of smart water

Table 5 shows the recovery factors of the tested waters from the core flooding model. As can be seen, the best result is related to smart water SMW. In contrast, the worst-case scenario is related to the 40000 ppm NaCl and the SW injection.

Recovery factor of CSMW

In this section, at first, the oil recovery of the core flooding in the secondary and tertiary stages will be presented, then the result of the pilot will be discussed.

Core scale

Secondary stage. Carbonated smart water (CSMW) in the core case recovered 14, 26.8, and 44.35% more oil than SMW, SW, and water with 40 000 ppm of NaCl, respectively (Fig. 6). Moreover, after the injection of one pore volume, CSMW recovered more oil than SMW and SW by 10, 24% in the core scale.

As shown in Fig. 6, the main oil volume has been produced before the breakthrough (BT), which is between 0.33 and 0.42 PV for all cases. The recovery factor's different values could be attributed to the sweep efficiency differences for several water types, as explained later in the mobility enhancement section. After the breakthrough, other mechanisms are triggered in addition to mobility enhancement. Those mechanisms are widely explained in the mechanisms part.

Tertiary stage. The ultimate oil recovery depends on which stage the carbonated water is injected. 2 PV seawater was injected into the core model as a secondary recovery stage. Then carbonated water was injected as a tertiary recovery after the plateau was reached in the previous SW. Fig. 7 depicted the recovery of the CSMW, SMW, CSW, and SW in the secondary and tertiary stages. The recovery factor in the secondary stage of the CSMW is higher than in the tertiary stage by 4%. As expected, results are consistent with reported coreflooding and modeling results of the nonfractured systems. (Mosavat & Torabi, 2014).

To examine which injected water is more effective, a comparison among the waters at a recovery factor of
80% is conducted in the secondary and tertiary stages. The CSMW recovered 80% oil after 0.7 PV injection compared to 2.4 PV of the CSW in the secondary stage. However, in the tertiary stage, 1.4 PV of CSMW was injected to recover the 80% oil after the SW, which could not be recovered even after 2.8 PV injection in the CSW case.

Pilot-scale
As in the core scale case, the CSMW proved more oil recovery in the extended pilot model than the SMW in the homogenous and heterogenous fractured and nonfractured cases with different values. The results are in agreement with Lee et al.\textsuperscript{5} homogenous model. The CSMW recovered 6.6 and 8% more oil than the SMW in the heterogenous nonfractured and fractured reservoirs, respectively (Fig. 8). While CSMW recovered 5.5 and 5% more oil than the SMW in the homogenous nonfractured and fractured reservoirs, respectively, as illustrated in Fig. 9.

The recovery increment after the breakthrough can be attributed to mechanisms such as viscosity reduction and mineral dissolution. As can be seen from Fig. 8, the breakthrough occurred at 0.6 PV. The very early breakthrough can be attributed to the high water's mobility in the channels (the fractures). Due to the bypassing of the oil by the water, only a small oil volume is recovered after the breakthrough in the nonfractured reservoir. A higher recovery is obtained in the fractured reservoir after the breakthrough due to
the CO₂ diffusion from the fractures into the matrices and the spontaneous imbibition process, where those mechanisms need a lengthy time to act effectively.

At the early time after the breakthrough, the recovery factor was high. This could be explained by the combined effects of the cocurrent and counter-current spontaneous imbibition flow regimes. However, the recovery rate starts to be less later due to the cocurrent spontaneous imbibition flow regime. Figure 9 shows that the fractures have a slight effect on the ultimate recovery, where both cases recovered almost the same ultimate oil recovery. The breakthrough occurred in the fractured reservoir earlier than the nonfractured one by 0.1 PV, but it recovered more oil after the BT than the nonfractured one as well. Based on the observation, the heterogeneity effect might explain the lower recovery of the heterogenous fractured reservoir.

**CO₂ storage**

Stored CO₂ amount has been obtained in the core and pilot models. In the pilot-scale scenario, 56 and 45.5% of the injected CO₂ has been stored in the fractured and nonfractured heterogenous reservoirs, respectively, as shown in Fig. 10. The same range was obtained in the experimental and modeling studies conducted by Lee et al.⁵ and Kechut et al.²⁰ in the homogenous reservoir. This difference in the trapped CO₂ can be attributed to the residual oil saturation in the fractured reservoir (15%), which is more than the residual oil in the nonfractured (10%) when CSMW is injected (Fig. 11).
Ion exchange

Ion exchange results obtained from the carbonated smart water injection have been compared with those obtained from smart water injection, as shown in Fig. 12. This study was applied to the fractured heterogeneous reservoir being the most imperative case in the carbonate reservoir. All of the divalent ions increase in both scenarios, SMW and CSMW, but with different values. Those simulation results are in agreement with the core test reported by Kilybay et al. However, the increase of Ca$^{2+}$ and Mg$^{2+}$ concentration is more pronounced in the CSMW. This increment could be attributed to the dolomite and calcite dissolution, as explained in the mineral dissolution and porosity changes section. The resulted SO$_4^{2-}$ is lower by 27.5% in the CSMW than the SMW. This reduction refers to the sulfate consumption in the processes that occurred in the CSMW, such as the electrical double layer expansion. SO$_4^{2-}$ replaces the adsorbed carboxylic group of the oil from the rock surface; consequently, it will be bonded with the positive charged divalent (Ca$^{2+}$ and Mg$^{2+}$), forming an electrical double layer.

Mineral dissolution and porosity changes

After injecting the smart water, the transportation of the modified ions to the rock minerals occurs by molecular diffusion. The system (rock...
minerals—formation water) is in an equilibrium state before injecting water changes this equilibrium. This, in turn, forms a concentration front, where at and behind those fronts, the chemical interactions take place. Those chemical interactions are either between the components in the aqueous phase (intra-aqueous reactions), which are fast and represented as chemical-equilibrium reactions, or between the minerals and aqueous components (slower), resulting in mineral dissolutions/precipitations and represented as rate-dependent reactions.

In several pilot cases, the pore volume increased in the pilot-scale by 2.5–5% in different cases. As shown in Fig. 13 and Table 6, mineral dissolution is more pronounced in the homogenous system than the heterogenous and fractured systems. This could be due to the consistency and uniformity of the fluid movement in the homogenous pores. The homogeneity allows the fluid to access all rock pores, thus providing contact with a larger specific surface area than the other cases. Furthermore, the contact time will be almost equal in all pores because of the regularly injected water front.

In the fractures and the high permeable part of the heterogenous rock, the fluids will move with low velocity in the large pores, and it will be in contact with...
fewer surface areas of the pores than the homogenous system. This leads to slight active reaction occurrence, leading to minor mineral dissolution values. This slow movement allows the system to reach the local equilibrium state and to the global equilibrium, but to some extent. In the homogenous pores, the fluid movement in the overall pores with relatively high velocity leads to a continuous renewal of the CSMW, resulting in continuous chemical reactions. These repeated actions do not allow the local or the global equilibrium to occur, thus more dissolved minerals. In the fractured system, the CSMW flows in the fractures and imbibes into the matrix. Therefore, the reactions will be active in the fractures more than the matrices; thus, the pore volume change and the mineral dissolution will be higher, as shown in Fig. 14.

In the fractured homogenous system, the reactions in the matrix (micropores) resulted in mineral precipitation. This precipitation is reflected mainly in the pore volume change, as can be seen in Fig. 15. This mineral precipitation has been observed experimentally at the core scale for carbonate reservoirs.4,47 However, no study has been reported for fractured reservoirs. The heterogeneity effect on mineral dissolution appears in this system, as shown in Fig. 14. In the fractured heterogenous reservoir, the
mineral precipitation in the micropores is compensated by the dissolution of the larger pores.

**Viscosity reduction**

The diffusion of the CO$_2$ into the oil reduces the viscosity, leading to mobility reduction and an enhancement of the sweep efficiency. In the pilot model, oil viscosity has been reduced by 63.5 and 70% in the matrix and fractures in the injector area after injecting 0.2 PV. In the producer area, oil viscosity reduction was 31 and 15% in the fractures and matrix. These values did not reach the same injector’s area values after injecting 1.5 PV because the irreducible oil saturation was not yet reached. Due to the high viscosity reduction, which cannot be reached in the SMWI, it could be concluded that viscosity reduction could be the primary factor affecting the oil recovery in the CSMW method.

**Mobility enhancement**

The carbonated water mobility will be lower than the conventional water mobility due to its high viscosity upon the CO$_2$ dissolution, almost around 10%. Based on the mobility equation (Eqn 31), the higher the water viscosity, the lower the mobility ratio, which means that the O-W front will be more stable, enhancing the sweep efficiency and leading to more oil recovery.

\[
M = \frac{K_{rw}}{K_{ro}} \frac{\mu_o}{\mu_w}
\]  

(31)

Where, $\mu_w$ = water viscosity, cp; $\mu_o$ = oil viscosity, cp; $k_{rw}$ = relative permeability of water; and $k_{ro}$ = relative permeability of oil.

Furthermore, CO$_2$ will reduce the viscosity of the oil, as explained in the viscosity reduction part. This reduction in the viscosity leads to a more enhancement of the mobility ratio, thus the sweep efficiency. Figure 16 depicts the breakthrough of the CSMW and SMW in the homogenous nonfractured pilot. It can be observed that the CSMW front is slower compared to SMW by 0.125 PV. Mobility change could be observed in the relative permeability curves change. For instance, at 60% water saturation ($S_w$), the water relative permeability ($K_{rw}$) decreases by 25%, and the water viscosity is increased by 10%; thus, the water mobility is decreased by 35%. Oil relative permeability increases by 15%, and simultaneously, the oil viscosity decreased by 40%, which resulted in two times oil mobility enhancement. The mobility ratio is decreased, consequently, by 32%.

**Wettability alteration**

Wettability alteration might be the result of several mechanisms acting in the CSMW injection. Mineral dissolution results in carboxylic oil components release with its adsorbed layer of the carbonate rocks. This process and the ion exchanges lead to a change in the rock wettability by replacing the divalent ion with oil on the rock surface and is magnified in the relative permeability curves. Besides, the reduction of interfacial tension and viscosity alteration of the water and oil due to CO$_2$ of carbonated water might substantially affect the wettability alteration. This change of wettability can be seen in Fig. 17 and 18 in the matrix and fracture.
Conclusion

In this work, the performance of CSMW for EOR and CO₂ storage in carbonate homogenous and fractured reservoirs was examined. The following conclusions have been obtained:

- Carbonated smart water injection has been demonstrated as a promising EOR method for naturally fractured carbonate reservoirs.
- CSMW recovered more oil than SMW, CSW, and SW in the core scale in both secondary and tertiary stages. In the pilot case: in the heterogenous reservoir (fractured and nonfractured) and the nonfractured homogenous reservoir, CSMW recovered more oil than SMW. In the fractured homogenous reservoir, SMW recovered more oil than CSMW until 0.6 PV injection. After 0.6 pore volume CSMW started to recover more oil than SMW.
- As a co-optimization method, 56 and 45.5% of the injected CO₂ have been stored in the fractured and nonfractured heterogenous reservoirs.
- Ions exchange and mineral dissolution processes could be important mechanisms to enhance oil recovery.
recovery in the CSMWI, where the pore volume increased.

- Viscosity reduction is one of the main mechanisms behind the oil recovery increment when the CSMW method is applied. CSMW decreased oil viscosity by 30–70%. The reduction of the oil viscosity enhanced the mobility ratio and thus the sweep efficiency in the system, leading to a like-piston displacement and late breakthrough time.

- Wettability alteration to more water-wet was observed when CSMW was used, leading to more oil recovery.

- A higher recovery is obtained in the fractured reservoir after the BT due to the CO₂ diffusion from the fractures into the matrices and the spontaneous imbibition process. Those mechanisms need a long time to act effectively and start paying off after the breakthrough.

- Diluted water or LSW injection cannot always be used like SMW, but the SMW has to be studied based on the formation water and minerals to find out the optimum smart composition.

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