CO₂ Storage in Low Permeable Carbonate Reservoirs: Permeability and Interfacial Tension (IFT) Changes During CO₂ Injection in an Iranian Carbonate Reservoir

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Abstract
The lack of fundamental experimental studies on low permeable carbonate reservoirs for CO₂ sequestration purposes is essential for further application of CO₂ sequestration as a highly-anticipated CO₂ mitigation method in deep saline aquifers, specifically those with low permeabilities. The core samples were taken from a carbonate reservoir in Iran and the brine composition was based on that of the same formation. The objective of this study is to investigate permeability alteration during CO₂ sequestration in the aquifers of a low permeable Iranian carbonate reservoir. Various parameters have been investigated. The effects of different parameters such as injection pressure, confining pressure, and temperature on permeability alteration of the cores was investigated. Moreover, the interfacial tension (IFT) of CO₂/brine was also determined at pressures and temperatures up to 7 MPa and 100 °C, respectively. The experimental results showed CO₂ solubility and rock dissolution to be the governing mechanism when CO₂ was injected into carbonate cores. The permeability measurements showed that permeability increases by increasing injection pressure and decreases by increasing confining pressure and temperature. The IFT measurement results showed that the IFT decreases significantly when there is an increase in pressure and temperature.

Keywords
low permeable, carbonate reservoirs, CO₂ sequestration, saline aquifer, Iranian reservoirs, IFT of CO₂/Brine

1 Introduction
Global warming is believed to be caused by an excessive consumption of fossil fuels. Over the past decade, CO₂ sequestration has gained considerable attention in the scientific community as a method to counteract the detrimental effects of global warming by safely storing large amounts of CO₂ in geological formations. Due to high occurrence and large storage capacity, aquifers are among the most suitable candidates for CO₂ sequestration. In this method, CO₂ is injected into deep saline aquifers, preferably more than 800 m deep, and stored in porous media via several mechanisms [1-4].

More than 50 % of the world’s hydrocarbon reservoirs are classified as carbonate reservoirs. Approximately 70 % of middle-east hydrocarbon reserves can be found in carbonate reservoirs [5]. Although there have been some preliminary studies for application of CO₂ sequestration in the Middle East, there still exists a huge gap in the literature regarding the application of this method in (low permeable) carbonate reservoirs specifically in Iran.

The injection of the CO₂ into the saline aquifers and the CO₂ interactions with formation brine and formation rock is important from two perspectives. Injected CO₂ reacts with formation brine and creates an in-situ weak carbonic acid, which dissolves formation rock. Further, CO₂ can react with formation rock that contains reactive metal ions such as calcium and magnesium to form different precipitates, for example, calcium and magnesium carbonates [6, 7]. The precipitation of minerals is favored at high pH values versus low pH values [8]. The four mechanisms of CO₂ sequestration have been widely discussed in previous studies. [3, 8, 9].

Numerous studies [9-15] have examined CO₂ sequestration in saline aquifers with a focus on CO₂ solubility trapping mechanisms. Their findings showed that CO₂ solubility is greatly influenced by CO₂ pressure, temperature,
and salinity. Some researchers reported findings of reduced permeability while others reported findings of increased permeability during CO₂ sequestration in saline aquifers. Information highlighting the density of CO₂ saturated brine, especially at reservoir conditions (high pressure and temperature), is crucial for determining the effectiveness of the CO₂ sequestration projects in saline aquifers. Literature survey on this matter revealed that, to date, limited work has been done specifically on carbonate reservoirs. The relationship between CO₂ solubility and its impact on the density of effluent brine and rock permeability is almost untouched in literature, hence the need for this study [14-19].

CO₂ injectivity is one of the major practical challenges during CO₂ injection into saline aquifers. In general, the parameters affecting well injectivity could be categorized as geomechanical effects, geochemical effects (precipitation and rock dissolution) and transport effects (fine mobilization) [20-24]. Rock and fluid interactions play vital role in changing the injectivity. Increasing the acidic strength of the formation brine via CO₂ dissolution in formation brine causes mineral dissolution and consequently increasing the permeability and injectivity. On the other hand, some of the minerals in solution could precipitate and block the pores, causing permeability impairment and reduced injectivity. In addition, salt precipitation may also occur during the injection of dry CO₂ into saline aquifers, causing reduced injectivity [25-29].

The study of Azin et al. [30] investigated CO₂ sequestration in carbonate aquifers with CO₂ pressure at 62 bar and temperature at 40 ºC for 91 days. Their experiments showed that porosity and permeability of dolomite cores increased during the process. This was due to dolomite dissolution with CO₂, which then resulted in an increase of the concentration of Ca²⁺ and Mg²⁺ in effluent brine. Recently, Jeddizahed and Rostami [31] investigated the effects of injection rate and brine salinity during CO₂ injection into sandstone cores. Their results showed that salt precipitation occurs during the early stage of CO₂ injection. Increasing the brine salinity also increased the salt precipitation level which resulted in 21-66 % permeability reduction. Salt precipitation decreases with an increase in the injection rates, which caused 43-62 % permeability reduction. Although the aforementioned study is very helpful to get an insight about the mechanisms of the process, the temperature of the experiments was not really representative of that of the aquifers. Izgec et al. [32] investigated the effects of CO₂ injection on changes of porosity and permeability of the carbonate cores using CT-Scan method. They studied the effects of different brine salinities, CO₂ injection rate and temperature. Experimental results showed that both permeability increase and decrease can be obtained, and this behavior is very case sensitive. In general, the major mechanism for permeability changes could be related to CO₂ solubility and rock dissolution. In general, CO₂ solubility and acidic strength are decreased with increasing the salinity and temperature. Fewer ions in solution means less rock dissolution, thus decreasing the permeability. Kovacs et al. [33] conducted a very detailed study on injection CO₂ sequestration on low permeable carbonates in which a great number of variables and their contribution were considered. They used numerical reservoir simulation and carbonate cores from previous experiments carbonate to investigate the effectivity and mechanism of sequestration. They stated that rock dissolution is a controlling mechanism during CO₂ injection to the carbonate reservoir. The pH of brine is lowered by the dissolved CO₂ in brine, which can dissolve carbonate rocks and alter permeability and porosity of the rock. Although the study is very comprehensive, the permeabilities studied were 100 and 10 mD; one can argue that those values are not really reflecting the mechanisms in low permeable range. In a simulation study, Ghafoori et al. [34] examined CO₂ injection to carbonate and sandstone aquifers. They concluded that permeability changes do not influence equilibrium regions and the only effect that permeability has is on the injectivity. They further stated that the mineral trapping capacity of sandstone aquifers is higher than the carbonate aquifers during the CO₂ sequestration process. Although most of the aforementioned studies were carried out on carbonate cores, the range of permeabilities were from 4 to 100 mD.

Another important factor that affects the sequestration mechanisms of CO₂ in geological formation is fluid-rock and fluid-fluid interfacial tension [15, 18]. The most important interfacial property is the interfacial tension (IFT) between CO₂ and brine that saturates the caprock and pre-exist in the aquifers/reservoirs. IFT controls the flow of multiphase fluids in the porous media. Laplace equation (Eq. (1)) is the most commonly used capillary pressure equation via which the entry level pressure in a cylindrical pore throat is calculated:

\[
P_e = \frac{2\delta_{w-CO_2} \cos \theta}{R}
\]

where \(\delta_{w-CO_2}\) is the interfacial tension between brine and CO₂, \(\theta\) is the contact angle between CO₂/brine/surface,
and R is the radius of the largest pore throat of the caprock that is accessible to CO$_2$/brine interface. Alternatively, IFT could be calculated using the capillary storage capacity of CO$_2$ [35]. The maximum column height, $H$, of CO$_2$ that can be trapped in a given formation is given by Eq. (2):

$$H = \frac{2\gamma_{\text{CO}_2} \cos \theta}{\rho_b - \rho_{\text{CO}_2}}$$

(2)

where $g$ is the acceleration of gravity and $\rho_b$, $\rho_{\text{CO}_2}$ the densities of brine and CO$_2$, respectively. IFT between brine and CO$_2$ has been experimentally measured in some of the previous studies [35, 36]. It can be seen that IFT is controlled by the thermodynamic conditions of the experiments, such as pressure and temperature, as well as salinity and composition of brine.

Aggelopoulos et al. [36] investigated experimentally the effects of various salts and salinity of brines on changes of IFT between CO$_2$ and brine. They found that the increase in IFT of CO$_2$ and brine composed of two salts (NaCl+CaCl$_2$) is the sum of the two individual IFT increments due to each salt. In order to evaluate the efficiency of any CO$_2$ sequestration project in geological formations, the knowledge of range of the IFT and its changes based on thermodynamic/geological configuration of the repository of interest is essential [3, 36].

To the best of the authors’ knowledge, no studies have been conducted on sequestration of CO$_2$ in very low permeable carbonate reservoirs, specifically in thermodynamic and geological conditions of Iranian reservoirs, where it can be observed that most of the literature focuses on simulation (often on field scale) [30, 31], or the experiments that are not really representative of geological conditions (pressure, temperature, salinity, pH) in low permeable carbonate aquifers [33].

The aim of the current study, therefore, is to investigate the feasibility of CO$_2$ sequestration in the aquifers of an Iranian carbonate oil reservoir. Since the major consequence of CO$_2$ dissolution in formation brine is permeability alteration via dissolution, this study also examines rock dissolution at a range of pressure, temperature and salinities. The effects of CO$_2$ injection pressure (1-7 MPa), formation rock confining pressure (5-15 MPa), temperature (27-100 °C), and salinity (119-294958 mg/kg) on rock permeability were investigated. In addition, the changes of IFT of CO$_2$/brine system under different pressure (1-7 MPa) and temperature (27-100 °C) conditions was experimentally investigated.

### 2 Experimental materials, setup and procedures

#### 2.1 Reservoir characteristics

The cores used in this study were taken from a mature reservoir called Gadwan, located in southwest Iran. A detailed composition of the reservoir fluids is presented in Table 1. The reservoir under observation has an edge type aquifer with a thickness of 25 m and an encroachment angle of 360 degrees. The average permeability of aquifers is about 4.93 mD and its porosity is about 18 % and the aquifer temperature is 100 °C. The initial aquifer pressure is about 21.95 MPa while the current pressure is 11.67 MPa. The pressure of the aquifer has declined because of crude oil production from the reservoir. By crude oil production, reservoir pressure declines, thus, water from aquifer encroaches into the reservoir to compensate the reservoir oil pressure. This will result in pressure decline in the aquifer.

#### 2.2 Fluids

Formation brine and sea water were used to represent the aqueous phase in this study. The total dissolved solids (TDS) of the formation brine was determined as 294,958 mg/kg (~30 wt. %) and sea water was determined as 35,079 mg/kg (3.5 wt. %). The components of formation brine and seawater are shown in Table 2. The formation brine was also collected from the aquifer in Gadwan.

| Components | Mole fraction (%) |
|------------|------------------|
| H$_2$S     | 0.00             |
| N$_2$      | 0.36             |
| CO$_2$     | 0.24             |
| C$_1$      | 22.92            |
| C$_2$      | 9.25             |
| C$_3$      | 7.70             |
| i-C$_4$    | 1.66             |
| n-C$_4$    | 4.80             |
| i-C$_5$    | 2.15             |
| n-C$_5$    | 3.10             |
| C$_6$      | 4.31             |
| C$_7$      | 4.62             |
| C$_8$      | 4.67             |
| C$_9$      | 4.40             |
| C$_{10}$   | 4.33             |
| C$_{11}$   | 25.49            |

| C$_{m}$, Mole weight |
|----------------------|
| C$_{m}$, Specific Gravity |
reservoir, which is also the same reservoir from which core samples were taken. In addition to what is presented in Table 2, the physical properties of the formation brine were also determined and the results are shown in Table 3. The analytical grade of CO$_2$ used for all the experiments were of 99.9% purity.

2.3 Core samples
The length and diameter of the core samples used in this study were 8.1 cm and 3.7 cm, respectively. Helium porosity and brine permeability methods were used to determine the average porosity and permeability of the core samples. Results showed the average porosity to be 16.27% and permeability to be 4.81 mD. Table 4 summarizes the dimensions and properties of the reservoir cores used. X-ray powder diffraction (XRD) was conducted on the cores to identify the composition of the rock. Density of the rock samples were measured to be 2.87 g/cm$^3$.

2.4 Apparatus
The schematic diagram of the coreflood setup used in this study is illustrated in Fig. 1. The main parts are a fluid accumulator, a core holder and a fluid collector. A syringe pump (ISCO 500D) with maximum working pressure of 25.85 MPa and maximum working flow rate of 200 cc/min was used to inject brine into the core samples. They were loaded into a high pressure stainless steel core holder that has a maximum operating pressure of 34.47 MPa. A back-pressure of 8.62 MPa was set at the back-pressure regulator. The differential pressures (DP) were then determined by using a pressure transducer. Following this, a liquid collector was deployed to collect the displaced brine and a gasometer was used to record the produced gas. The entire setup was placed inside an oven that has a temperature controller which allows for constant temperature experiments. The temperature, differential pressure and injection pressure were recorded with a data acquisition system and a computer.

For IFT measurement experiments, IFT400TM with the maximum operating temperature of 205 °C and 21 MPa was used, as shown in Fig. 2. The pendant drop method was used to measure the IFT of the CO$_2$ and brine at reservoir conditions. A 50 cm$^3$ stainless steel chamber, with a glass window, was provided for taking the photographs. The IFT is then determined through the drop shape

| Components | Formation brine (mg/kg) | Seawater (mg/kg) | Fresh water (mg/kg) |
|------------|-------------------------|-----------------|---------------------|
| Na$^+$     | 107873                  | 11100           | 14                  |
| K$^+$      | 2219                    | -               | 1                   |
| Ca$^{2+}$  | 4342                    | 419             | 14                  |
| Mg$^{2+}$  | 536                     | 1304            | 3                   |
| Sr$^{2+}$  | 338                     | -               | <1                  |
| Ba$^{2+}$  | 1                       | -               | 1                   |
| Cl$^-$     | 177051                  | 19350           | 15                  |
| HCO$_3^-$  | 257                     | 146             | 37                  |
| SO$_4^{2-}$| 2342                    | 2690            | 33                  |
| Br$^{-}$   | -                       | 70              | <1                  |
| TDS        | 294958                  | 35079           | 119                 |

| Properties | Value             |
|------------|-------------------|
| Salinity (mg/kg) | 294,958          |
| Water viscosity (cp) | 0.586          |
| Water compressibility coefficient (MPa$^{-1}$) | $3.10 \times 10^{-4}$ |
| Density at reservoir condition (g/cc) | 1.16            |
| Formation volume factor (bbl/STB) | 1.017           |
| Specific gravity | 1.139           |

| Properties | Value |
|------------|-------|
| Length (cm) | 8.10  |
| Diameter (cm) | 3.70  |
| Bulk volume (cm$^3$) | 87.09  |
| Pore volume (cm$^3$) | 14.17  |
| Porosity (%) | 16.27  |
| Permeability (mD) | 4.81  |
analysis technique. This is administered through an image processing code written by LabVIEW.

2.5 Experimental procedure

After the core samples were cleaned, dried and weighted, they were placed into the core holder. The initial air permeability is then measured at the ambient condition. The core holder was then vacuumed for 24 h. Afterwards, the formation brine was injected into the core and the brine permeability was measured accordingly. The permeability measurements were repeated three times and the uncertainties of the results were calculated to have an expanded relative uncertainty of 1.2 % with a coverage factor of 2.

The oven temperature was increased to 100 °C and maintained for about 12 h. Following that, the core samples were pressurized to 10 MPa by brine injection. Different pore volumes of the CO₂ with controlled constant injection rates (1-7 MPa) were injected into the core samples. After the injection, the core samples were depressurized and the oven temperature was reduced to ambient temperature. The injectivity reduction of the core samples was evaluated by injecting air into the core samples. Air permeability was then determined at the remaining water saturation (Sₜₙ) level. These experiments were repeated by changing the different parameters such as different temperatures (27-100 °C), different injection pressures (1-7 MPa), and different confining pressures (5-15 MPa). The effect of the brine types on permeability was investigated by using three different brines which comprise formation brine, sea water and fresh water. After the experiments were completed, the effluent brine was collected and sent for further analysis. The pH value of each collected brine sample (including all the three types of brine used) was measured accordingly. Finally, the concentration of the calcium present in the effluent formation brine was measured by using inductively coupled plasma optical emission spectrometry (ICP-OES).

To measure the IFT, the entire system was initially checked for leakage with deionized water. It was then cleaned with acetone and deionized water before being flushed with nitrogen and evacuated [14]. At each pressure and after drop formation, a period of 600s (seconds) was needed to ensure thermodynamic equilibrium between the two phases [37, 38]. During this interval, IFT drops rapidly and then is stabilized by the same phenomenon that has been reported in a number of previous studies. [11, 15, 17, 18, 39, 40]. Before each measurement, a complete saturation of CO₂ and brine was achieved by injecting both phases to the cell and shaking them to reach an equilibrium condition of saturation. Then, the two equilibrium phases were separated at constant temperature and pressure. The density of each separate phase was accurately measured using an Anton PAAR digital high-pressure density meter. The equilibrium brine was extruded through the needle in the pendant drop apparatus, which was surrounded by equilibrium gas. Adequate time (10-12 h) was given to each solution to reach equilibrium condition and the IFTs were then determined accordingly. Drop sizes and shapes were also recorded from the visible segment of the sight cell. The uncertainties in IFT measurement were calculated to have an expanded relative uncertainty of 1.47 % with a coverage factor of 2. The expanded relative uncertainty of density was found to be 1.2 % with the coverage factor of 2.

3 Results and discussions

3.1 Effect of injection pressure on permeability

It is believed that CO₂ injection into brine saturated cores affect core permeability [30, 41-46]. Thus, different injection pressures (1-7 MPa) at the constant confining pressure of 10 MPa and temperature of 100 °C were applied. Core permeability was then determined. Each test was conducted using fresh water, formation brine and sea water. The results are presented in Fig. 3. The error bars showed 5 % of deviation from fresh water results.

The experimental results showed that the increasing injection pressure had a significant impact on core permeability. Clearly, core permeability increases with the increasing injection pressure. Moreover, it was observed that permeability was affected by salinity. At constant injection pressure, core permeability was higher in fresh water injection, followed by sea water injection and finally, formation brine injection. Taking the injection pressure of 1 MPa as an example, it was observed that permeability was 4.29 mD, 2.98 mD and 2.32 mD when fresh water,
sea water and formation water were injected, respectively. In addition, at constant injection pressure of 7 MPa, permeability was determined to be 7.62 mD when fresh water was used, 7.24 mD when sea water was used and 5.69 mD when formation brine was used. Permeability reduction during CO$_2$ sequestration in aquifers is believed to be caused by salt precipitation, which results in reduced injectivity. It should be noted that in practical situations, it is very unlikely that fresh water is used for injection due to fiscal considerations, and injection of formation water is both technically and economically a more interesting option. It can be observed that using formation brine instead of freshwater in similar conditions of injection results in an average of 35 % reduction in permeability.

Permeability enhancement is caused by rock dissolution during CO$_2$ sequestration in aquifers. CO$_2$ solubility and reactivity increases with pressure. Previous studies have pointed out that a decrease in pH of the brine can be observed as the dissolution of CO$_2$ in brine is elevated by pressure, which creates a favorable condition for rock dissolution to occur [11, 47-50]. Therefore, in order to link the changes of permeability to the rock dissolution, the pH of effluents as well as calcium concentrations had to be determined after each coreflood experiment. Fig. 4 illustrates the pH of effluent brine and calcium concentration versus variable injection pressures at constant confining pressure of 10 MPa and 100 °C.

It can be seen from Fig. 4 that solution pH decreased with an increased injection pressure for all three types of brines used. However, this reduction was more severe when fresh water was used. This study suggests that CO$_2$ solubility is affected by several parameters, one of which is salinity. CO$_2$ solubility in fresh water was higher than in saline waters and this had resulted in a lower pH with fresh water [18, 48]. The latter can be observed in Fig. 4, where solution pH values was the highest in the formation brine, followed by sea water and finally fresh water.

As was discussed earlier, rock permeability increases with an increased pressure due to enhanced CO$_2$ solubility and increased rock dissolution. This inherently resulted in higher concentration of the Calcium cations in the effluent brine. As can be observed from Fig. 4, Calcium concentration increases with the increasing pressure regardless of type of the brine. This demonstrates that injection of CO$_2$ commences a chemical reaction between aqueous and solid phase. The mechanism of the reaction can be explained as follows. As CO$_2$ is injected, it dissolves in brine and produces carbonic acid. Then, carbonic acid dissociates into two components namely: hydrogen and bicarbonate ions, which results in drop of pH in solution (Eq. (3)). Finally, hydrogen ions attack the rock and dissolve it (Eq. (4)). Therefore, the amount of Mg$^{2+}$ and Ca$^{2+}$ ions increases in a solution. The mechanisms of dissolution of carbonates in aqueous solutions has been adequately discussed in previous studies [51, 52]:

$$\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}^+(aq) + \text{HCO}_3^-$$  \hspace{1cm} (3)

$$\text{CaMg(CO}_3)_2 + 2\text{H}^+(aq)\leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$$ \hspace{1cm} (4)

Moreover, the reduction in effluent pH is another indicator of increase in the concentration of carbonate ions in the brine or, in other words, higher solubility of CO$_2$ in
Brine as pressure is increased. The decrease in solution pH with pressure has been reported in previous studies, both in carbonate and sandstone rocks [15, 50, 53].

Figs. 5 and 6 show the XRD image of the samples before and after the experiments, respectively. The peak at 29.5º illustrates the main composition of the clean rock sample (before any experiments) is dolomite CaMg(CO$_3$)$_2$ (2-5 wt. percent accuracy). It can be observed that the injection of CO$_2$ into the rock did not cause any change in the composition of the rock i.e. no CO$_2$ mineralization can be observed. The absence of CO$_2$ mineralization mechanism could be justified by pointing out that the reaction rate coefficient of CO$_2$ mineralization in carbonate rocks is considerably low, consequently the time scale required for this mechanism to naturally occur, without using any catalyst or any additional methods such as pH swing, is very long, in order of thousands of years [3, 50, 51]. Therefore, in the current study, the changes in mineralogy of the sample is assumed to be negligible.

### 3.2 Effect of confining pressure on permeability

The effect of confining pressure on rock permeability was investigated under the confining pressure of 5-15 MPa at a constant injection pressure of 1 MPa and 100 °C. The brines tested were fresh water, sea water and formation brine. Fig. 7 displays the permeability changes with the variable confining pressures. The error bars show 5 % deviation from formation brine permeability. Regardless of the brine used, permeability reduced with the increased confining pressure. The lowest permeability was achieved under 15 MPa confining pressure and the highest permeability was accomplished under 5 MPa confining pressure. This trend is consistent in all the three tested brines (fresh water, sea water and formation brine). Nonetheless, brine type appears to affect rock permeability.

At constant operating condition (temperature and pressure), rock permeability was higher with fresh water, followed by sea water and finally, formation brine. At a constant confining pressure of 5 MPa, rock permeability was 4.87 mD with fresh water; 3.95 mD with sea water, and 3.26 mD with formation brine injection. These values reduced to 2.30, 1.85, and 1.33 mD, respectively, when under 15 MPa confining pressure. It can be observed from Fig. 7 that regardless of injection pressure, confining pressure significantly affects the reduction in permeability. As confining pressure increases, a reduction of 50 %, 53 %, and 60 % can be observed for fresh water, seawater, and formation brine, respectively. It can also be inferred from the results that the effects of confining pressure on reduction of permeability becomes more pronounced at higher salinities.
Confining pressure directly affects the effective stress-induced anisotropic tortuosity. Increasing the anisotropic tortuosity decreases the permeability. At constant injection pressure, increasing the confining pressure also increases the effective stress on the rock mass, which consequently reduces the pore space and caused rocks to shrink. This eventually increases the rock mass tortuosity for CO$_2$ movement, thereby resulting in reduced effective CO$_2$ permeability in the rock mass [47-51].

3.3 Effect of temperature on permeability of carbonate cores

Fig. 8 presents the permeability changes with respect to the different temperatures of 27, 38, 66, and 100 °C at the injection pressure of 1 MPa and a confining pressure of 10 MPa. Fig. 9 displays the effluent pH and calcium concentration versus temperature at constant injection pressure of 1 MPa and a confining pressure of 10 MPa. It seems clear that CO$_2$ solubility is the governing mechanism for rock dissolution during CO$_2$ sequestration in the aquifers. CO$_2$ solubility is reduced by increasing the temperature from 27 to 100 °C. This creates unfavorable conditions for rock dissolution. CO$_2$ solubility is also dependent on salinity where the higher the salinity, the lower the CO$_2$ solubility [54-56].

As shown in Fig. 8, permeability is reduced by increasing the temperature from 27 to 100 °C for all the three tested brines. The error bars in the Fig. 8 show 5% deviation from permeability in fresh water. As expected, permeability is higher when fresh water was used as opposed to sea water and formation brine injection, respectively. The values decreased to 4.29, 2.98, and 2.32 mD, respectively, when the temperature was increased to 100 °C. The relationship between solution pH and CO$_2$ solubility is shown in Fig. 9 where increasing the salinity causes the CO$_2$ solubility to reduce significantly. This also reduces the acidic impact of CO$_2$. The pH measurement results also show that pH increases as temperature was increased; this can be explained by the reduced CO$_2$ solubility as temperature increased. At constant temperature, the highest pH was noted in the formation brine injection but the lowest pH was noted in fresh water injection. The outcome is due to the negative impact of salinity on CO$_2$ solubility. The impacts of composition and salinity of brines have been discussed in detail in the previous works on CO$_2$ solubility in brines [18, 57, 58].

The amount of Calcium collected in the effluent core samples (see Fig. 9) also decreases as the temperature is increased. This also indicates that temperature adversely affects CO$_2$ solubility and rock dissolution.

3.4 Permeability changes with pressure, temperature and salinity

It is believed that rock dissolution during CO$_2$ injection into carbonate reservoirs is the major mechanism for permeability alteration. Rock dissolution is directly related to CO$_2$ solubility in water, in which the higher the CO$_2$ solubility, the higher the rock dissolution and the higher the permeability. Pressure, temperature, and salinity are the major parameters that affect CO$_2$ solubility and rock dissolution during CO$_2$ injection. By increasing the pressure, CO$_2$ solubility increases and then the solution become
more acidic. Consequently, rock dissolution increases, which results in a higher permeability with pressure. On the other hand, CO$_2$ solubility is reduced with temperature. This means, the acidic strength of the solution decreases with temperature, resulting in a less rock dissolution and less permeability with temperature. In addition, CO$_2$ solubility is reduced with salinity. Therefore, acidic strength and rock dissolution are reduced too, which results in lower rock dissolution and permeability with salinity [54, 56-58]. In brief, permeability is enhanced by increasing the pressure. On the other hand, decreasing the salinity and temperature increases the permeability.

3.5 Effects of temperature and pressure on IFT of CO$_2$-brine

Fig. 10 shows the effect of pressure (1-7 MPa) on the dynamic IFT, up to 2000s, hereafter stated in s, of formation brine with CO$_2$ at a constant temperature of 100 °C. Moreover, the changes in IFT, brine and CO$_2$ density with pressure and temperature are shown in Table 5. It can be observed that the IFT between brine and CO$_2$ decreases initially and after 600s reached a semi-plateau and after nearly 900s an equilibrium is achieved regardless of the pressure. The possible reason behind the decrease in IFT before 900s could be attributed to mutual dissolution of the two phases (CO$_2$/brine). The similar duration to achieve equilibrium (depending on the salinity of brine) has been reported in work of other researchers as well [35, 36].

The IFT data also shows that at any isotherm, increasing the pressure results in reducing the IFT between CO$_2$ and brine, hereafter referred to as IFT. The IFT decreased significantly by increasing the pressure from 1 to 7 MPa. The minimum and maximum IFTs of 20.15 and 37.56 mN/m were achieved under the injection pressure of 7 and 1 MPa, respectively. At low pressures, the decrease of IFT is noticeably sharper in comparison with those of higher pressures. The rate of IFT reduction is diminished at longer periods of time and reaches a plateau at around 900s at all the temperature series as can be seen in Figs. 10 and 11. The above mentioned behavior can be observed for all the isotherms. As an example, the changes of IFT versus time for various pressures at constant temperature of 100 °C is shown in Fig. 10.

On the other hand, increasing temperature had a different impact on the IFT of brine and CO$_2$ as shown in Fig. 11. Increasing the temperature negatively impacted the IFT, and resulted in an increase in IFT at constant injection pressure of 1 MPa. The minimum and maximum IFTs of

| Temperature (°C) | Pressure (MPa) | Brine density (g.cm$^{-3}$) | CO$_2$ density (g.cm$^{-3}$) | IFT (mN/m) |
|-----------------|----------------|-----------------------------|-----------------------------|------------|
| 27              | 1              | 1.211                       | 0.018                       | 25.96      |
| 27              | 2              | 1.180                       | 0.039                       | 24.18      |
| 27              | 3              | 1.130                       | 0.063                       | 23.92      |
| 27              | 4              | 1.140                       | 0.092                       | 22.17      |
| 27              | 5              | 1.152                       | 0.128                       | 20.43      |
| 27              | 6              | 1.156                       | 0.183                       | 19.50      |
| 27              | 7              | 1.161                       | 0.710                       | 18.80      |
| 38              | 1              | 1.101                       | 0.017                       | 30.96      |
| 38              | 2              | 1.109                       | 0.037                       | 29.16      |
| 38              | 3              | 1.118                       | 0.059                       | 28.12      |
| 38              | 4              | 1.131                       | 0.084                       | 25.91      |
| 38              | 5              | 1.136                       | 0.115                       | 24.12      |
| 38              | 6              | 1.142                       | 0.153                       | 21.15      |
| 38              | 7              | 1.145                       | 0.207                       | 19.33      |
| 66              | 1              | 1.067                       | 0.016                       | 35.83      |
| 66              | 2              | 1.071                       | 0.033                       | 29.95      |
| 66              | 3              | 1.089                       | 0.052                       | 27.88      |
| 66              | 4              | 1.084                       | 0.073                       | 25.18      |
| 66              | 5              | 1.109                       | 0.096                       | 24.02      |
| 66              | 6              | 1.116                       | 0.124                       | 21.42      |
| 66              | 7              | 1.121                       | 0.141                       | 19.9       |
| 100             | 1              | 1.126                       | 0.014                       | 37.56      |
| 100             | 2              | 1.153                       | 0.031                       | 35.70      |
| 100             | 3              | 1.186                       | 0.045                       | 33.97      |
| 100             | 4              | 1.190                       | 0.062                       | 29.63      |
| 100             | 5              | 1.193                       | 0.082                       | 26.93      |
| 100             | 6              | 1.195                       | 0.912                       | 23.97      |
| 100             | 7              | 1.198                       | 0.12                        | 20.15      |

Fig. 10 Dynamic IFT of formation brine and CO$_2$ at constant temperature of 100 °C.
25.96 mN/m and 37.56 mN/m were achieved under 27 and 100 °C, respectively.

It is also important to note that as temperature is increased, solubility of CO$_2$ in brine is reduced and therefore the IFT is adversely affected (increased). At 1MPa pressure, the CO$_2$ is at liquid state. Therefore, the solubility of CO$_2$ in brine is not very significant as compared to that of in supercritical state [3, 59, 60]. As a result, it can be seen that the changes in IFT values due to the reduction in dissolution is more dominant than the increase in IFT from temperature rise. Consequently, the IFT is reduced as temperature is increased at low pressures (below the critical point).

CO$_2$ solubility in brine is the governing mechanism when controlling the IFT of formation brine and CO$_2$. The higher the CO$_2$ solubility, the lower the IFT. CO$_2$ solubility in brine increases by increasing the pressure and decreases by increasing the temperature. As shown in Fig. 10, the minimum IFT of formation brine and CO$_2$ was achieved under the highest pressure of 7 MPa and the lowest IFT was achieved under the minimum pressure of 1 MPa. However, when it comes to the effect of temperature on IFT, the total entropy of two phase surface and entropy changes served as the primary governing mechanism while CO$_2$ solubility remains as the secondary mechanism. Increasing the temperature increases the mobility of the molecules and the kinetic energy. Thus, the total entropy of the two phase surface increases. This results in lower free energy (ΔG). Consequently, it lowers the IFT through temperature [61, 62].

Another observation noted from the drop analysis and IFT measurements is the shape and volume of the analyzed brine drops. Fig. 12 shows the typical images of the pendant drops under different pressure and temperature conditions. Fig. 12(a) presents brine drop under 1 MPa pressure (IFT is 37.56 mN/m), Fig. 12(b) presents brine drop under 7 MPa pressure (IFT is 20.15 mN/m), Fig. 12(c) presents brine drop under 27 °C temperature (IFT is 25.96 mN/m) and Fig. 12(d) presents brine drop under 66 °C temperature (IFT is 35.38 mN/m). As can be observed, the changes in the drop shape and volume are apparent. This is because of the CO$_2$ dissolution in brine decreases the IFT, hence resulting in bigger size drops and higher volumes.

The implication of the above results for practical sequestration projects is that the interaction between CO$_2$ and formation brine during CO$_2$ injection phase in aquifers, and the CO$_2$ displacement by invading brine during the CO$_2$ migration (imbibition) phase is controlled by pressure, temperature and composition of formation brine in the repository of interest [62-64]. Due to the effects that these primary variables have on the IFT between CO$_2$ and aquifer brine, which in turn affects capillary pressure and relative permeability, the effects of each of those parameters needs to be studied in detail for the repository of interest.

The current study can be enhanced in future by taking into account the effects of salinity and brine composition on changes of IFT and CO$_2$ solubility in carbonate reservoir. Moreover, longer time frames of the experiments on
permeability alternation could be beneficial in observing the extent to which mineralization (mineral carbonation) occurs as CO₂ is injected to reservoirs/aquifers.

4 Conclusion
This study has investigated the effectiveness of CO₂ sequestration in the aquifers of an Iranian carbonate oil reservoir. Changes in rock permeability, viscosity and density of CO₂ saturated brines, and the IFT of CO₂ and brine were determined experimentally. The following conclusions could be drawn from the investigation conducted:

1. CO₂ solubility and consequently rock dissolution increased with pressure and decreased with temperature and salinity.
2. Permeability was increased with increasing CO₂ pressure regardless of the types of brine used. Under 1 MPa injection pressure, permeability was 4.29, 2.98, and 2.32 mD with fresh water, sea water, and formation brine, respectively. The values increased to 7.62, 7.24, and 5.69 mD, respectively, under 7 MPa pressure.
3. Permeability was reduced by increasing confining pressure. The lowest permeability was achieved under 15 MPa confining pressure and the highest permeability was accomplished under 5 MPa confining pressure.
4. Permeability was reduced by increasing the temperature from 27 to 100 °C for all the three tested brines. However, permeability was higher when fresh water was used as compared to sea water and formation brine.
5. Density of effluent brine decreased with increasing temperature. Brine density decreased from 1.1511 to 1.1261 g/cc by increasing the temperature from 27 to 100 °C.
6. The IFT decreased by increasing the pressure from 1 to 7 MPa. The minimum and maximum IFTs of 20.15 and 37.56 mN/m were achieved under the injection pressure of 7 and 1 MPa, respectively.
7. The IFT increased by increasing the temperature from 27 to 100 °C. The minimum and maximum IFTs of 25.96 mN/m and 37.56 mN/m were achieved under 27 and 100 °C, respectively.
8. CO₂ dissolution in brine decreases the IFT, hence resulting in bigger size drops and higher volumes.

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