CO₂ wettability behavior during CO₂ sequestration in saline aquifer - An Experimental study on minerals representing sandstone and carbonate

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Abstract

Changes in wettability have been quantified by measuring the CO₂ contact angle on some selected minerals typical for reservoir rocks – quartz, calcite and feldspar, in the presence of brine at reservoir conditions – by use of the captive-needle drop method. Also wettability alteration of the CO₂ as a function of time was investigated.

No significant change in contact angle was observed for any of the minerals as function of pressure and only small variation with change in temperature and salinity. All mineral surfaces remained strongly water-wet. A minimum in contact angle was observed at 36 °C near the critical pressure, which could be related to the near-critical behavior of the CO₂-phase. Exposing the calcite mineral to CO₂ for 50 days at fixed conditions did not cause any significant change in water wettability.

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1. Introduction

Wettability is the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids [1]. Wettability is one of the important factors that control the efficiency of the CO₂ geological storage process. In CO₂ injection process into aquifer, it determines the fluid distribution in the reservoir. In a typical aquifer, for CO₂-brine system, the rock is usually water wet and water is the preferred phase to occupy the small pores and to contact most of the rock surface. Any decrease in water

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wettability of the rock could eventually increase the tendency of CO₂ to wet the rock surface. In such a case, CO₂ will occupy the small pores and will be present in the largest pores as a film on the rock surface. The existence of such a film may affect the petrophysical properties of the reservoirs and therefore the injectivity level of a reservoir formation [2]. On the other hand, in the caprock, possible changes in wettability due to physical-geochemical processes could possibly decrease the capillary entrance pressure. Such a decrease could reduce the sealing integrity of the caprock which is one of the major factors that control the safety of geological CO₂ storage. This paper presents changes in wettability quantified by measuring the CO₂ contact angle on some selected minerals typical for reservoir in the presence of brine at reservoir conditions.

Water-wettability of various inorganic (e.g., stainless steel) [3] and organic (coal and shale) materials [4], [5] have been found to change in the presence of dense CO₂. Some of these studies are referred to in the following. Chiquet et al. reported that the wettability of minerals mica and quartz, in the presence of CO₂ at elevated pressures, changed from water wet to intermediate wet [5]. Shah et al. did the same experiments and observed that the wettability alteration of mica was moderate and that the wettability of quartz and ‘real’ caprock substrate was not altered [6]. Bikkinia claims that exposure of calcite and quartz to dense water-saturated CO₂ caused a permanent shift in the contact angle [7]. Plug et al. found increase in CO₂ wettability of medium-rank and high-rank coals for increasing CO₂ pressure [4]. A similar change from water-wet to intermediate wet conditions upon increase in pressure was reported by Siemons et al. for coal-water-CO₂ systems [8].

Egermann et al. observed that CO₂ was clearly the non-wetting phase in carbonate cores for pressures from 80 to 180 bar and temperatures from 60 to 80 °C [9]. Experiments by Wollenweber indicated that repeated CO₂ exposure resulted in a reduction of the capillary sealing efficiency [10]. Chalbaud et al. showed by use of pressurised micromodels that for water/CO₂ system, the CO₂ can wet a solid surface at reservoir conditions if the surface is intermediate wet or oil-wet [2], [11]. Hildenbrand et al. performed breakthrough experiments on pelitic rocks and showed that the capillary-sealing efficiency of the samples depends on the gas phase used in the experiments [12].

To sum up, different results are presented in literature from experiments conducted under different conditions, which makes direct comparison difficult. Hence, further systematic investigations are needed.

Contact angle measurement is the most reliable measurement method for wettability estimation of surfaces when studying pure fluids on flat surfaces [13]. Contact angle measurement is performed by establishing the tangent angle of a liquid drop with a solid surface at the base and makes use of Young’s Equation (1). It is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions (see Figure 2.1), solid-vapor, γₛᵥ, solid-liquid, γₛｌ, and liquid-vapor, γₗᵥ [14], [15]:

\[ γₛᵥ\cos \theta_γ = γₛ𝑙 - γₗᵥ \]  

Equation (1)

Here \( \theta_γ \) is the Young contact angle and the angle is measured through the CO₂ phase. In CO₂-brine system when a drop of CO₂ is placed on a mineral surface in the presence of brine, typical scenarios are as follows:

- \( \theta_γ = 180° \), completely water wet
- \( \theta_γ ≈ 90° \), intermediate or neutral wettability
- \( \theta_γ < 90° \), predominantly CO₂ wet and if \( \theta_γ > 90° \), predominantly water wet
- \( \theta_γ = 0° \), completely CO₂ wet
One classic technique for measuring contact angle is the captive bubble method. A captive bubble of the less dense fluid is injected beneath the surface immersed in the denser liquid. The surface is supposed totally hydrated so that between the solid and the bubble exists a thin layer of water [16], [17]. Among the methods that have been developed to measure contact angles, axisymmetric drop shape analysis (ADSA) methods are giving the best accuracy, simplicity, and versatility [18]. ADSA-P is a technique to fit the meridian of an experimental drop to the theoretical drop profile according to the Young–Laplace equation [15], [19].

In this paper, changes in wettability have been quantified by measuring the CO₂ contact angle on some selected minerals typical for reservoir rocks in the presence of brine at reservoir conditions. We present a set of CO₂ contact angle data on representative reservoir minerals at pressure, temperature and salinity conditions relevant for a CO₂ storage operation. Results are also presented for CO₂ wettability alteration as function of time.

2. Minerals

The minerals was chosen for contact angle measurement are, quartz, feldspar and calcite. The minerals quartz and calcite are representative of sandstone minerals and chalk rocks respectively. Feldspar is the most common rock-forming mineral (about 60% of the earth’s crust). The all three minerals are strongly water-wet in the presence of oil and air [20]. To minimize any roughness effect on contact angle measurements, substrate surfaces were well polished. To clean the quartz and feldspar substrates, they were first washed with a Deconex cleaning detergent solution under ultrasonic bath for 20 minutes, then washed with distilled water, then rinsed with a 6 % nitric-acid solution while heated to 30 °C and finally washed with distilled water [21]. Calcite surface could be destroyed with any kind of acid. For this reason, to clean the calcite mineral, it was washed with Deconex solution under ultrasonic bath and rinsed with distilled water at the end. Prior the experiment, substrate cleanliness was checked by measuring air-water-mineral contact angle. A drop of distilled water was placed on the substrate surface at room conditions and the criterion used for sufficiently clean crystal was contact angle in water phase less than ~10 °.

3. Experiment

Measurements have been carried out in a range of pressures extending from atmospheric pressure up to 400 bars, for two different temperatures, 36 °C and 66 °C with pure water and water with 0.2 and 0.8 NaCl molarities. The experiments were performed by the captive needle drop method. The experimental setup is equipped with a high-pressure viewing cell with two parallel see-through windows, in which drops of CO₂ are formed at the end of a needle and contacted with the substrate (mineral) immersed in
brine. The CO₂ drop is positioned beneath the substrate to avoid the gravity effect. The angle was always measured through the CO₂ phase. Moreover, wettability alteration of the CO₂ as a function of time was investigated. For this purpose, the calcite mineral was exposed to the CO₂ drop at 100 bars and 36 °C in the presence of saline water for 50 days.

3.1 Experimental setup

The experiments were carried out in a cylindrical high-pressure cell (volume 45 cm³) of stainless steel with two see-through sapphire windows. The cell was rated for maximum working pressure and temperature respectively 850 bar and 180 °C. The cell was heated by heating wire wound around its cylinder surface and insulated by sheets of closed-cell silicone-rubber sponge. Figure 2 gives a schematic view of the experimental set-up and shows a CO₂ drop prepared for image analysis. The images recorded by the camera are transferred to a computer. The software (Attention Theta 4.1.0) calculates contact angle and drop volume by fitting the Young-Laplace equation (or polynomial equations) to the shape of the drop.

![Figure 2: Schematic view of the experiment and the captured drop image showing the contact angle](image)

At first, when the drop is formed on the substrate surface, the CO₂-brine-mineral contact line length (length AB in Figure 2) is constant over a range of contact angles and drop sizes. When the triple line starts moving, the resulting contact angle is taken as the true advancing contact angle.

3.2 Experimental procedure

The contact angle for brine-CO₂-substrate system was measured at constant temperature, specific water salinity and increasing pressure for each substrate. The procedure for measuring contact angles was as follows:

1. Cell was cleaned and substrate was mounted in the cell.
2. The cell was evacuated through port number 5.
3. Water or brine was drawn into the cell through port number 2 from a reservoir glass bottle (not the buffer cylinder). When the cell was filled, the valve at port 2 was again switched to the buffer cylinder.

4. Then CO\textsubscript{2} was injected into the cell through port number 1. The cell was pressurized to specified pressure by injecting more brine from buffer cylinder and CO\textsubscript{2} from CO\textsubscript{2} pump. Part of injected CO\textsubscript{2} will dissolve in the brine depending on pressure, temperature and brine salinity. To ensure that the water phase was saturated by CO\textsubscript{2}, injection to the cell was continued until a small gas cap had formed. The cell temperature was set either at 36 or 66 °C.

5. Afterwards, a new CO\textsubscript{2} drop was slowly introduced to the substrate and a few hours were allowed for phase equilibration at desired pressure and temperature.

6. Then drop images were recorded by a camera with a pixel resolution of 512×480 and analyzed by use of computer software.

7. CO\textsubscript{2} contact angle was measured at various pressures in the range from atmospheric pressure to 400 bar, constant temperature and specific water salinity (fresh water, 0.2 and 0.8 NaCl molarities). Afterwards, the cell was depressurized and cleaned by fresh water and methanol and dried with CO\textsubscript{2} gas. For new set of measurement, either for higher temperature or new water salinity, procedures 1 to 7 were repeated.

4. Experimental results

Results are presented for CO\textsubscript{2} contact angle on the surface of quartz, feldspar and calcite measured as function of pressure at two different temperatures, 36 and 66 °C, and for three different salinities. In addition, change in CO\textsubscript{2} contact angle on calcite at constant conditions of pressure, temperature and water salinity is presented as a function of time.

4.1 Calcite

Contact angles were measured at 36°C for pressures ranging from 3 to 400 bar for fresh water and 0.8 M NaCl brine (Figure 3). Except near critical pressure, no significant change was observed in water-wettability with increasing pressure, assuming typical measurement uncertainty ± 2°. Increasing the salt concentration has only minor effect on CO\textsubscript{2} wettability. Figure 4 shows CO\textsubscript{2} drops on calcite surface while the cell was filled with fresh water and brine with 0.8 M NaCl brine at 36°C. It is clear that, at these conditions, calcite was strongly water wet.

Prior the experiment, the calcite surface was polished to make it smooth enough for measuring contact angle, but at the end of measurements, the calcite surface was found to be etched. Dissolution of CO\textsubscript{2} in water forms a weak carbonic acid which dissolved some parts of the calcite surface and made it heterogeneous or non-smooth. To avoid spurious effects on measurements from surface roughness, we polished the calcite surface at the end of each set of tests. An X-ray diffraction test showed that there were no mineralogy changes of the calcite after its surface was etched by dissolution in CO\textsubscript{2} saturated brine.
Figure 3: CO$_2$–brine contact angle on calcite surface for fresh water and 0.8 M NaCl brine at temperature 36 °C

Figure 4: CO$_2$ drop on calcite surface in the presence of Upper) fresh water, Lower) 0.8 M NaCl brine

4.2 Quartz

Measured contact angle for the brine-CO$_2$-quartz system is shown in Figure 5. Similar to the case of calcite no significant change in water wettability was observed with increasing pressure. Increasing the salt concentration had only minor effect on CO$_2$ wettability. However, increasing the temperature from 36
°C to 66 °C decreased the CO₂ contact angle by 8-14° depending on pressure. Such a decrease is significant and it should be noted that no such decrease in contact angle was observed for feldspar, which is a related silica mineral. The cause of the temperature effect has not been identified. Figure 6 shows images of CO₂ drop on quartz surface for fresh water at two different temperatures, 36 °C and 66 °C. At similar pressure, quartz is less water wet at 66 °C than at 36 °C.

![Figure 5: CO₂-brine contact angle on quartz surface versus pressure](image)

For fresh water, T=36 °C

- P= 5 bar, T=36 °C, θ= 170°
- P= 20 bar, T=36 °C, θ= 169°
- P= 62 bar, T=36 °C, θ= 166°
- P= 75 bar, T=36 °C, θ= 167°
- P= 105 bar, T=36 °C, θ= 169°
- P= 150 bar, T=36 °C, θ= 170°
- P= 205 bar, T=36 °C, θ= 170°
- P= 400 bar, T=36 °C, θ= 170°
4.3 Feldspar

Similar to calcite and quartz, no significant change was observed in CO₂ contact angle upon increase of pressure from atmospheric to 400 bar. Neither did increase of temperature change the contact angle. Increasing the salt concentration resulted in slightly smaller water wettability. The results for the brine-CO₂-feldspar system are presented in Figure 7 for two different temperatures and different salinities.

Similar to calcite and quartz, a characteristic minimum in CO₂ contact angle is observed near 75 bar at 36 °C, while for 66 °C this is much weaker or possibly absent. The minimum coincides with the critical pressure for CO₂ (73.8 bar), but the temperature is 5 °C higher than the critical temperature. The reduced compressibility of CO₂ is a good estimator for the proximity to the critical point, going towards infinity at the critical point (73.773 bar, 30.9782 °C). The reduced compressibility \( C_{r,CO₂} \) at 36 °C and 66 °C as function of pressure, plotted in Figure 7, was obtained by Equation (2):

\[
C_{r,CO₂} = \frac{(d\rho/dp)}{(P_c/\rho_c)} \tag{2}
\]

Here, \( \rho \) is CO₂ density calculated by an EOS of Span and Wagner [22], \( P_c = 73.733 \) bar, CO₂ critical pressure, and \( \rho_c = 467.527 \) kg/m³ is CO₂ critical density.

A relatively strong anomaly in CO₂ reduced compressibility is observed at 36 °C, 5 °C above the critical point, while at 66 °C this is weak, indicating that the observed minimum may be related to the near-critical behavior of the CO₂-phase.
Figure 8 shows CO₂ drop on feldspar surface in the presence of fresh water and 0.2 M NaCl brine at T=36 °C and for 0.8 M NaCl brine at T=66 °C. There is no significant change in contact angle with change in pressure and temperature, but the contact angle decreased by 4.5° degrees at the higher salt concentration.

Figure 7: Contact angle as function of pressure for the brine-CO₂-feldspar system and reduced CO₂ compressibility as function of pressure
To investigate wettability alteration with time, the calcite mineral was exposed to the CO₂ drop at 105 bar and 36 °C in the presence of saline water for 50 days (Figure 9). The contact angle decreased by 3° during the first few days and afterwards remained constant. The initial sharp decrease could be due to heterogeneities on the calcite surface caused by calcite dissolution in the water phase.

**Figure 9: Contact angle as function of time for brine-CO₂-calcite system at 105 bar and 36 °C**
Figure 10 shows CO₂ droplets on the calcite surface at different points of time:

![Image showing CO₂ droplets on calcite surface at different time points](image)

**Figure 10:** CO₂ drop on calcite surface in 0.8 M NaCl brine over 50 days

According to these observations, the water wettability of the calcite mineral did not change significantly at the time scale of the laboratory experiment and was still strongly water wet at the end of the test.

5. **Conclusion**

- No significant change in contact angle as function of pressure was observed for CO₂ drop on the surface of quartz, feldspar and calcite. Increase of salt concentration made feldspar slightly less water-wet whereas no significant change was observed for calcite and quartz. Increase of temperature from 36 °C to 66 °C made quartz less water-wet whereas no similar effect was observed for calcite and feldspar.
- A minimum in contact angle near the critical pressure was observed at 36 °C for all three minerals feldspar, calcite and quartz. A relatively strong anomaly in CO₂ compressibility is observed at 36 °C, less so at 66 °C, indicating that the observed minimum may be related to the near-critical behaviour of the CO₂ phase.
- Exposing calcite mineral to CO₂ for 50 days at fixed conditions showed that the water wettability of the calcite mineral did not change significantly at the time scale of the laboratory experiment.
- Despite small variations in measured contact angles all three minerals quartz, feldspar and calcite remained strongly water-wet throughout the experiments described in this paper. This indicates that sandstone and carbonate saline aquifers could be strongly water wet in the presence of CO₂ and in geological storage conditions. However, to come to a firm conclusion, it may be required to perform analyses on real reservoir rock samples because the wettability could depend on the presence of other minerals and/or microstructure of the mineral surfaces in the
pore system. For such analyses other methods such as Amott/USBM tests might be better suited than contact angle measurement.

- No significant change was observed in water wettability of calcite at laboratory time scale. This indicates that long term CO₂ exposure might not change reservoir properties such as relative permeability characteristic, capillary entry pressure and residual non-wetting phase saturation.

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Reference


