

WETTABILITY OF COMMON ROCK-FORMING MINERALS IN A CO₂-BRINE SYSTEM AT RESERVOIR CONDITIONS

John Mills, Masoud Riazi and Mehran Sohrabi
Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh, U.K.

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ABSTRACT

Wettability plays a major role in subsurface fluid migration, however little empirical evidence besides qualitative relative permeability data in this context is known about the characteristics of carbon dioxide (CO₂). Core analysts use several methods combined for use in the oil industry, including the USBM (U.S. Bureau of Mines) method and Amott test, supported visually by images from an environmental scanning electron microscope (ESEM) at near-vacuum conditions. Unlike contact angle measurements between CO₂ and brine, the combined methods cannot readily utilize CO₂ at supercritical state which is crucial for understanding sequestration phenomena. Air-brine in those tests is considered as the analogue, which may not be appropriate.

As a part of an ongoing investigation into CO₂ sequestration, this work focuses on evaluating the wetting state of CO₂ at reservoir conditions with contact angle measurements. There is limited consensus among experimentalists in this field, and conclusions are drawn from a limited data set. This paper provides further observations to leverage the assessment of CO₂ wettability.

We have extended prior investigations in a cross-disciplinary manner by preparing pure mineral samples of common rock forming minerals consisting of quartz, orthoclase, labradorite, calcite and biotite. These were benchmarked against processed quartz and mica plates which are commonly used for this type of test. This method may also be of benefit to the Petroleum industry for investigating how wettability varies with mineralogy; aiding the development of improved chemical design for enhanced oil recovery.

The contact angle of CO₂ through the brine phase was measured using the captive bubble technique for plain and carbonated brine. Brine carbonation did not show a significant difference in CO₂ contact angles. The findings of this investigation between 800-2000 psi at 40°C show strongly water-wet to water-wet conditions for all the gas and supercritical measurements of CO₂. Our measured data shows that the mica and calcite substrates become more water-wet as pressure is reduced, whereas the quartz and biotite substrates become more water-wet by pressurizing the system. A comparison of the measured

contact angles for N_2 and CO_2 shows that CO_2 is less water wet than N_2 at low pressure conditions. There is not a clear trend at high pressure conditions.

We have identified a challenge, which is that supercritical CO_2 cannot be irrefutably characterized by the Amott-USBM method, and propose that contact angle measurement is the most appropriate direct observation of wettability. A novel extension to this method has been developed to provide insight into the workings of realistic reservoir minerals.

INTRODUCTION

Saline aquifers and depleted gas fields have been identified for use as repositories for anthropogenic carbon emissions produced from sources such as coal and gas-fired power plants [1]. Projects currently demonstrating the CO_2 injection process include Gorgon, Australia; In Salah, Algeria; Weyburn-Midale, Canada; Sleipner West, Norway and many others which are in the planning or early-operational phase. The projects utilize the two types of geological formations deemed most suitable for storage: depleted gas fields and saline aquifers. These formations are generally located at depths greater than 700m subsea where pressure and temperature conditions cause CO_2 to form a dense, supercritical (liquid-like) state. A major advantage of injecting into saline aquifers is that they are widespread and can handle a large injected volume of CO_2 , although they are not as well characterized as gas fields.

Although the caprock is thought of as the primary seal to prevent unwanted migration, CO_2 may also be rendered immobile through capillary trapping. This has been the focal point of several recent core flooding studies of sandstones and carbonates [2-4] and recently reviewed by Müller (2010) [5]. Additional CO_2 is sequestered as it dissolves into formation water creating a dense, carbonated phase. Reservoir simulators suggest that density driven currents may form and even enhance CO_2 trapping [6, 7], however the process has not been verified experimentally at reservoir conditions. Over thousands of years, CO_2 precipitates as a solid carbonate mineral and is the most secure form of storage. This has been replicated in small quantities experimentally [8, 9]. The competition of these trapping mechanisms is important, as it allows us to determine the best strategy to safely and economically inject and secure CO_2 within the reservoir with a low probability of unwanted migration. Capillary trapping is one of the important mechanisms for safe storage. This mechanism, which takes place partly during the injection process and over time as a result of dissolution trapping, is a function of the interfacial tension (IFT) between CO_2 and brine, and the wettability of the reservoir rock (i.e. the contact angle of the CO_2 -brine-rock system). Investigating the wettability (and interfacial tension) therefore, is a significant step towards understanding the physics relating to capillary trapping.

At the laboratory scale, there are several methods available to quantify wettability, though we lack a standard procedure that has been suitably benchmarked across industry (such as the recent centrifuge study by the Society of Core Analysts) [10]. The measurement of wettability can be divided into quantitative methods such as the

combined USBM (U.S. Bureau of Mines) and Amott [11, 12] methods, and contact angle measurement where a more idealized system may be used [13]. For the purpose of investigating the wettability of CO₂, the combined method requires spontaneous imbibition tests and the centrifuge to be utilized. This is not strictly appropriate for studying supercritical CO₂ behavior unless air is assumed as a suitable analogue for supercritical CO₂. Large differences in relative permeability end-points for CO₂-brine have been measured during coreflooding but have not been convincingly explored yet with respect to conventional systems [2, 3].

We conducted contact angle and IFT measurements to better understand the fundamental wetting properties of CO₂ at subcritical and supercritical conditions, which were benchmarked against N₂ to determine whether the two were comparable despite the expected differences in IFT [14]. The limited set of published works in this research area means that there is not a definitive consensus on the wetting nature of CO₂.

THEORETICAL BACKGROUND

Fundamental wetting behavior in an ideal system is described by the balance of forces in the Young-Dupré equation: $\sigma_{SL} - \sigma_{SV} + \sigma_{LV} \cos \theta = 0$, where σ is the interfacial tension between the solid-liquid (σ_{SL}), solid-vapor (σ_{SV}) and liquid-vapor (σ_{LV}) phases. This equation has been adapted and applied elsewhere [15] to enable a more integrated exploration of contact angle, interfacial tension and line tension. The impact of short-range electrostatic and van-der-waals interactions on crude oil-brine-rock interactions has been found to be dependent on experimental conditions [16].

From literature, different drop (bubble) delivery methods and embedding fluids have been used, making direct comparison difficult [8, 17-19]. To replicate the storage formation, brine has been used as the embedding phase and CO₂ as the injection fluid. The captive bubble technique was used for this study to respect the buoyant nature of the CO₂ drop (bubble) being injected (Fig. 1). Alternatively, the needle can be oriented in the downward direction, which would enact a downward force from the needle and not allow a free CO₂ bubble to be measured. The techniques for drop delivery are discussed vigorously in the realm of colloid science [20] and part of this investigation is directed towards emphasizing this strong link between core analysis and surface chemistry.

Espinoza and Santamarina (2010) report a water-wet regime between CO₂-brine (200g NaCl/kg) where the contact angle oscillates close to 40° as the gas pressure is increased in the chamber [8]. Their results indicate that for a calcite substrate there was little difference between brine and distilled water at low pressure, but at supercritical conditions distilled water preferentially wet the surface compared to brine (~10° difference). An oil-wet quartz plate showed intermediate wettability, tending to water-wet at CO₂ liquid conditions.

Chiquet *et al.*, (2005, 2007) report different wetting regimes for mica including intermediate wetting behavior [18, 19]. They highlight that their needle orientation (i.e.

top to bottom) is less appropriate for low pressure, buoyant CO_2 ; they claim there was no difference between needle orientations at 100 bar although they have not described the bubble size used for comparison which is important. We have respected the buoyancy effect of the drop phase to facilitate suitable benchmarking of tests. They report contact angle results for three different brine conditions (0.01, 0.1 and 1 M NaCl) using processed quartz and mica substrates. Contact angle varied from 0-20° for low pressure mica (data for 0° was not shown) and 20-30° for quartz. At 100 bar (1450psi) 60-80° for mica and 40-55° for quartz was reported, although there is some variance with the brine salinity.

Dickson *et al.*, (2006) illustrates a change in wetting conditions with CO_2 pressure on chemically treated glass slides [21]. Using water as the drop phase and CO_2 as the embedding phase, at 1 bar pressure, the 12% SiOH (silanol) surface was intermediately water-wet (95-100° through the water phase) and upon pressurization with CO_2 , the contact angle increased to approximately 160° indicating CO_2 -wet conditions.

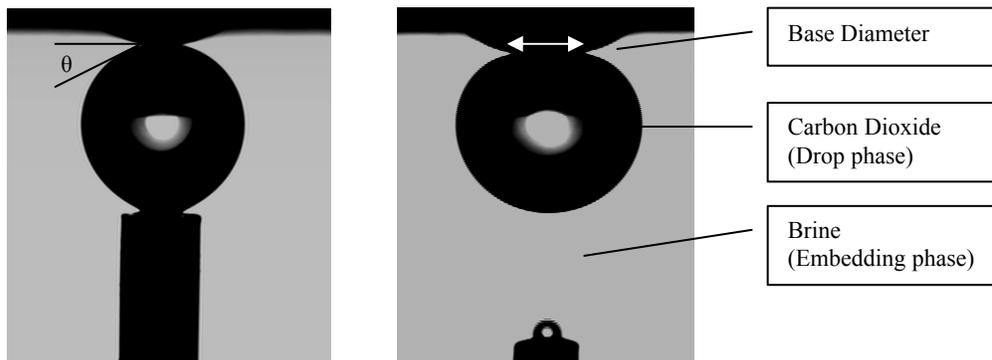


Figure 1: Bubble of buoyant CO_2 surrounded by denser fluid (brine). On the left is the static captive bubble (SCB) method and on the right is the dynamic captive bubble (DCB) method. Needle diameter is 0.793 mm.

EXPERIMENTAL FACILITIES

High-Pressure High Temperature Contact Angle Measurement Rig

The drop shape analyzer (Fig. 2 and 3) is capable of contact angle and IFT measurements up to 7,500 psi and 180°C, for various configurations.

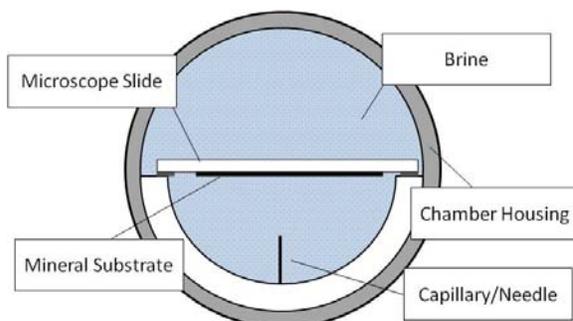


Figure 2: Cross-section view of measurement chamber (not to scale)



Figure 3: Photograph showing purge lines and injection ports connected to chamber

Fluids and Materials

Two commercially produced plates and five raw mineral samples (Table 1) were used in this study. The manufactured plates are optical-grade quartz and mica. Although quartz is a dominant mineral in sandstone reservoirs, mica is considered a minor constituent (except in mudstones) and both are unlikely constituents in carbonate rock formations. These processed minerals are compared with their ‘raw’ counterparts: quartz and biotite (mica) in addition to three other pure mineral samples obtained from hand specimens: orthoclase (alkaline) and labradorite (calcic) feldspar, and calcite. Brine was used as the embedding phase in this study made up to 35000 ppm salt; nitrogen and carbon dioxide are used as the drop phase (properties in Tables 2 and 3). Toluene, methanol, isopropanol, acetone, distilled water and brine were used to clean or prepare surfaces. Nitrogen and carbon dioxide were used to purge lines as appropriate prior to use.

Table 1: A diverse group of minerals were chosen for the study, which are drawn from various rock types

MINERAL	EMPIRICAL COMPOSITION	LIKELY OCCURANCE
Quartz	SiO ₂	Sandstones, Shale
Biotite (Mica)	KMg _{2.5} Fe ²⁺ _{0.5} AlSi ₃ O ₁₀ (OH) _{1.75} F _{0.25}	Shale, minor in sandstones
Orthoclase (Alkaline Feldspar)	KAlSi ₃ O ₈	Sandstone/shale
Labradorite (Calcic Feldspar)	Na _{0.4} Ca _{0.6} Al _{1.6} Si _{2.4} O ₈	Minor in sandstones/shale
Calcite	CaCO ₃	As a cement, Carbonates

Table 2: Fluid densities at 40°C (313.15 K) at pressures used in this study

FLUID	PRESSURE (psi [bar])	DENSITY (kg/m ³)
Brine	800 [55]	1020.3
Carbon Dioxide	800 [55]	130.6
Nitrogen	800 [55]	59.2
Brine	1900 [131]	1023.4
Carbon Dioxide	1900 [131]	745.3
Nitrogen	1900 [131]	137.5

Table 3: Major brine components

ION	ppm
Cl	18200
Na	11700
SO ₄	3180
Ca	1170
Mg	326
K	123

EXPERIMENTAL PROCEDURE

Surface Preparation

The preparation of the processed plates and mineral samples differed. The lighter, more fragile mica plate was bonded to a sterile, trimmed microscope slide using epoxy, whereas the quartz plate could be used ‘as is’ within the environmental chamber. A glass weight was placed on top of the substrate to prevent any disturbance during brine injection. Samples were initially cleaned in toluene, methanol, acetone and isopropanol before first use, and thereafter rinsed in methanol, distilled water and placed in an ultrasonic bath in a beaker of brine prior to testing.

Mineral hand samples were bonded to glass and polished using a modified thin section preparation technique [22]. Initially, we chose hematite in addition to the aforementioned minerals; however it could not be effectively trimmed and polished. Biotite mica was too fissile for lapping, so layers were carefully cleaved from the surface and glued to a sterile microscope slide.

Contact Angle Measurement

The rig was initially prepared by cleaning all the lines with cycles of toluene, methanol and acetone before first use; we allowed each of the abovementioned solvents to diffuse for several hours into dead-end volumes contained within the apparatus. Nitrogen followed by distilled water cleared the lines of any remaining chemicals. During testing, brine was de-gassed overnight and between tests such that no gas bubbles could be seen to exsolve from the water.

Tests were conducted for carbonated (CB) and plain brine (PB) to investigate the effect of dissolved CO₂ on CO₂ wettability. A procedure was developed to ensure conditions could be replicated repeatedly. Both static and dynamic captive bubble (drop) methods were used with CO₂ and N₂ for comparison. A high-pressure cell was filled to 1600psi and connected to a pair of very accurate pumps via Hastelloy (C-276) lines and fittings. The injection lines were bled with CO₂ or N₂ as required, and the chamber was evacuated and filled with brine to 300-1000 psi (for setting up low and high pressure tests respectively) before switching on the heating jacket to 40°C (313.15 K). Upon pressure stabilization, CO₂ was injected at a rate of 5cc/hr to a pressure slightly above the target pressure. Brine was withdrawn at 0.2 psi per second to pull CO₂ through towards the needle, whilst allowing it to reach thermal equilibrium for several minutes. When a CO₂ bubble entered the chamber, it was recorded using high-speed video as it was brought towards the substrate. Pressure was maintained by balancing CO₂ injection and brine withdrawal. In the case of the static captive bubble method, the bubble was allowed to equilibrate with the surface before an advance-recede cycle was performed. For the dynamic captive bubble method, the CO₂ bubble was injected to the point of release from the needle tip and IFT measured. To prepare carbonated brine, the chamber was purged with CO₂ to 800 psi (55.16 bar) and filled with brine above the substrate. The system was further pressurized by injecting to the gas-cap as needed and left overnight (>12 hours) until the pressure had clearly stabilized. CO₂-injection was carried out as before. The interfacial tension was measured at the point of bubble release for CO₂-brine and Nitrogen-Brine systems. There are clearly many variations of the methods of preparation, which we would invite a standard to be determined.

DATA ANALYSIS AND DISCUSSION

Contact Angle Test results

Contact angle results are presented for various mineral substrates under carbonated (CB) and plain conditions (PB). The contact angle (θ) is measured through the brine (embedding phase) where $\theta < 60^\circ$ is considered to be water-wet, $60^\circ < \theta < 120^\circ$ is considered intermediate-wet and $\theta > 120^\circ$ is considered gas-wet (drop phase). Contact angles reported are average values between the left and right side of the drop and have been rounded to two significant figures for clarity. Advancing angles are reported with respect to the CO₂ drop advancing (water receding); receding angles refer to the CO₂ drop being retracted into the needle (water advancing). Unless stated explicitly, contact angles are published for CO₂ advancing. For the drop delivery method, we refer to the

static captive bubble method where the gas bubble is held in a fixed position against the substrate and advance-recede measurements of the CO₂ bubble are performed. The dynamic method refers to a bubble which detaches fully from the needle and comes to rest against the substrate; interfacial tension (IFT) is measured using this technique.

1. Benchmark Quartz and Mica against literature data

Given that a major aim of this work is to supplement existing published data, an initial benchmark for this work was required. Plain and carbonated brine were used to represent initial injection of CO₂ into the formation, and post-closure respectively. The dynamic captive bubble was used for the quartz plate. For sub-critical CO₂ (840 psi, 58 bar) using plain brine, the (CO₂) advancing contact angle (measured through the brine phase) ranged from 38-40° (minimum to maximum) for base diameters of 1.606-2.711 mm. The contact angle (27-38°, 1.574-2.025 mm) was lower for supercritical CO₂ (1892 psi, 130 bar). These tests show a decrease in contact angle tending towards water-wet conditions when the pressure increases as reported by Espinoza and Santamarina (2010) [8]. Figure 4 shows results using the dynamic captive bubble (DCB) method for carbonated brine on quartz and mica plates. For quartz, we obtained a range in contact angles between 27-32° where base diameter varied between 1.266-2.338 mm at supercritical conditions (1871 psi, 129 bar). At supercritical conditions for mica, we saw water-wet conditions (35-43°) using the dynamic method and carbonated brine; with an average value of 38.9°. Figure 4 shows CO₂ injected into carbonated brine using the static captive bubble method (SCB); the average contact angle was more water-wet (34°) for base diameters 1-1.6 mm. Chiquet *et al.*, (2005) report intermediate wetting behavior for mica: ~70° at 100 bar [18].

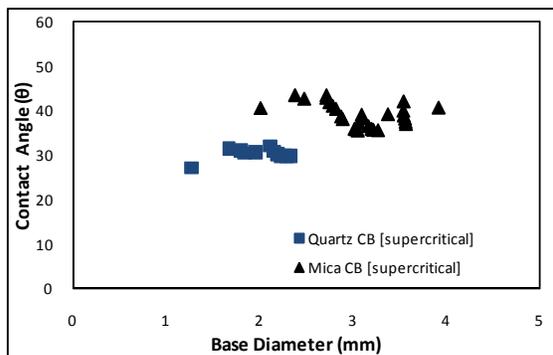


Figure 4: Quartz and mica in carbonated brine using the dynamic captive bubble method for CO₂.

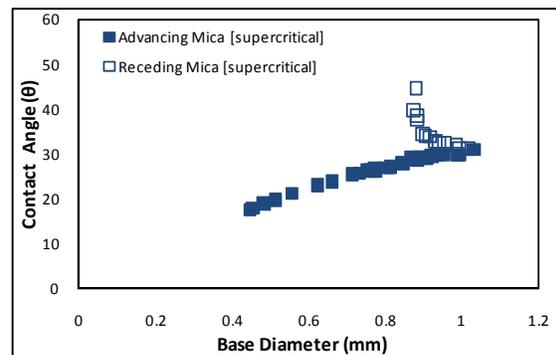


Figure 5: Mica plate in plain brine using the static captive bubble method for supercritical CO₂.

2. Raw mineral counterparts

The main focus of this study is to investigate the behavior of naturally occurring minerals (biotite, calcite, orthoclase and labradorite) in a CO₂-brine system – in addition to evaluating different drop methods for future measurement. We benchmarked mineral quartz against the processed quartz plate. Subcritical CO₂ gave a marginally higher contact angle on the quartz mineral 42-45° than the quartz plate 39-40°. Carbonated brine tests were conducted for calcite and orthoclase.

The SCB method for carbonated and plain brine is shown for calcite (Fig. 6). We observed low hysteresis ($\theta < 3^\circ$) in the advancing and receding angles, and that brine carbonation did not affect the result. Figure 6 also shows a range of contact angles as the bubble is deployed across the surface; stationarity is observed at about 1 mm base diameter. Figure 7 shows a maximum difference of 13° between Orthoclase at plain and carbonated brine conditions; the system remains water-wet. Espinoza and Santamarina (2010) report $30\text{-}40^\circ$ for subcritical CO_2 for a drop of water resting on a calcite substrate at 21.85°C (295K) [8]; comparably, we observed $25\text{-}28^\circ$ at 838 psi (58 bar), albeit at a higher temperature. Our maximum advancing contact angle (27°) using the SCB method at 828 psi (57 bar) falls within the same wetting regime as they reported. We observed dissolution of the calcite surface local to the CO_2 droplet when using plain brine, due to a local drop in pH at the mineral surface. Widespread etching was observed when the brine was carbonated. Differences in the wetting nature of the minerals tested may be explained by the free energy of the mineral surface, although we may also need to take into account the role of pH and salinity as before for crude oil-brine-rock interactions [15].

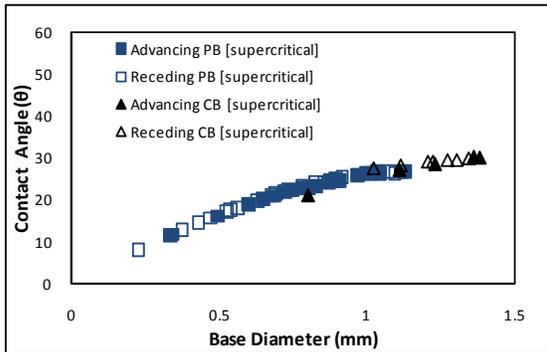


Figure 6: Comparison of CO_2 -Brine-Calcite with carbonated (CB) and plain brine (PB) using the static captive bubble (SCB) method

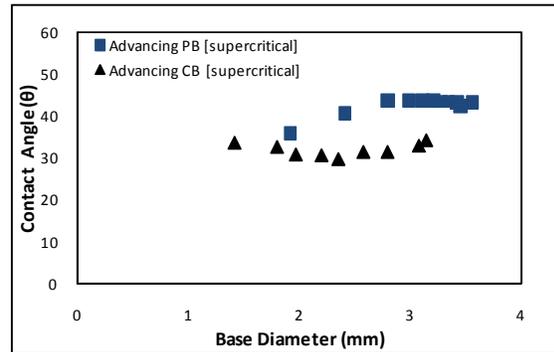


Figure 7: Comparison of CO_2 -Brine-Orthoclase with carbonated (CB) and plain brine (PB) using the dynamic captive bubble (DCB) method

3. Comparison of N_2 and CO_2

We compared the contact angles for CO_2 and N_2 at similar pressures using the SCB and DCB drop delivery methods. The impact of carbonated versus plain brine was also measured. Figure 8 shows little difference in the contact angles for N_2 and CO_2 as the bubble size is increased using the SCB method. At a base diameter of 1 mm, N_2 (1903 psi, 131 bar) and CO_2 (1905 psi, 131 bar) have a contact angle of 28° and 26° respectively. Using plain brine, CO_2 has a narrow range of contact angle values ($35\text{-}38^\circ$, 1.574-2.109 mm) which are marginally higher than N_2 at similar conditions ($32\text{-}35^\circ$, 1.258-2.089 mm). Orthoclase had a larger difference (13°) between carbonated and plain brine; a similar trend is observed for the quartz plate (Fig.9). In both cases, carbonating the brine had the effect of making the surface more water-wet. All measured data is plotted in Figure 10; data points are displayed as a range to account for different drop delivery methods. Nitrogen and carbon dioxide are comparable at both high and low pressures for tests run at 40°C . Differences occur mainly due to the method of bubble delivery.

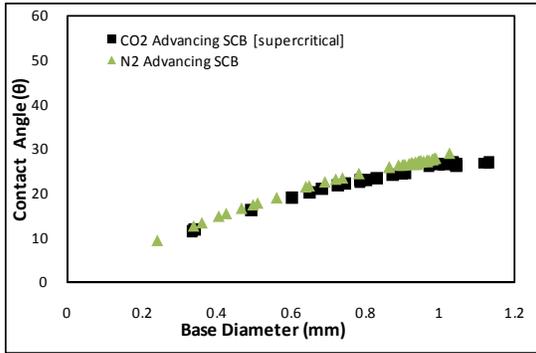


Figure 8: N₂ and supercritical CO₂ advancing angles on calcite using plain brine and SCB method

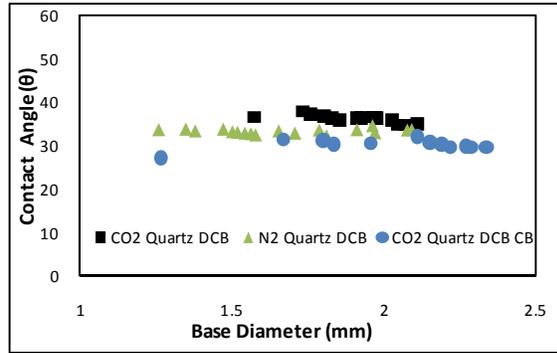


Figure 9: N₂ and supercritical CO₂ on a quartz plate with plain and carbonated brine (DCB method)

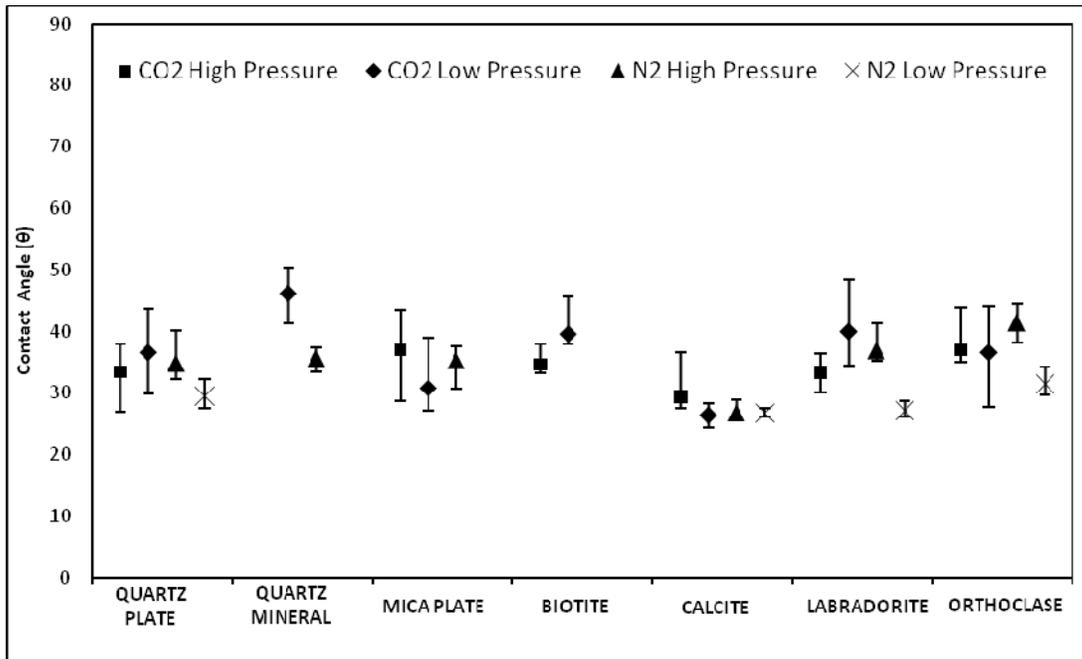


Figure 10: Contact angle measurements compiled for all conditions tested [plain, carbonated, static (advancing) and dynamic] at 40°C. The average has been weighted based on currently available data

4. Effect of drop delivery method

Prior work on the effect of drop delivery method and base diameter indicates that the choice of delivery method does impact the contact angle value; which is further exacerbated by surface roughness [20, 23, 24]. For the static captive bubble method, we fixed the distance between the substrate and the needle tip for all the tests, to ensure that the same bubble size was being delivered to the substrate regardless of the pressure or fluid conditions. We measured a non-linear increase in contact angle using the static captive bubble method for base diameters less than 1mm. They tended to approach stabilization as they increased in size; this effect has also been observed for crude oil measurements [25]. Chiquet *et al.*, (2005) showed a similar effect: injecting and withdrawing a CO₂ bubble at 35 bar (approx. 0.7-1.0 mm base diameter) yields multiple contact angles with a difference of ~40° [18].

IFT results

We used an extended formulation for calculating brine density at pressure and temperature [26] and obtained gas density information from the National Institute of Science and Technology, USA. Our measured values for CO₂-brine at low (42.5±2.5 mN/m) and high (29.1±1.2 mN/m) pressure are comparable to the trend reported by Bachu and Bennion (2009)[27].

Part of this work is to compare the properties of N₂ with CO₂ to account for any similarities or differences between the gases at the same conditions. To our knowledge, no data on nitrogen-brine contact angle or interfacial tension have been reported for reservoir brines at 40°C. It has been reported elsewhere that nitrogen IFT ranges from 69.36 (145 psi, 10 bar) to 59.82 (4351 psi, 300 bar) in degassed water, which decreases further as either CH₄ or CO₂ are added in increasing concentrations to the gas stream [14]. We measured $\sigma_{lg} = 67.1$ mN/m for nitrogen at 854 psi, which decreased at a higher pressure to 61.2 mN/m at 1906±5 psi (130 bar). Our observations agree with the decreasing trend reported for the nitrogen-water system.

Several issues regarding the type and quantity of dissolved salts were raised by Chalbaud et al., (2006) [28]; concentrations of salts such as MgCl₂ and CaCl₂ can raise the CO₂-brine interfacial tension, which highlights the importance of formation water sampling. The clear difference in IFT values between CO₂ and N₂ at similar conditions indicates that a more systematic investigation of the salinity and temperature effects on CO₂, N₂ and CH₄ is required.

CONCLUSIONS

- We observed strongly water-wet to water-wet regimes for advancing carbon dioxide and nitrogen drops (bubbles) at subcritical and supercritical conditions on reservoir minerals.
- Increasing the pressure made CO₂ more water-wet for biotite, labradorite and the quartz plate and less water-wet for the mica plate and calcite mineral.
- The average contact angle for high pressure N₂ was comparable to supercritical CO₂ on calcite and the quartz and mica plates.
- Under laboratory conditions, there was little difference in contact angle between carbonated and plain brine for the substrates tested. Orthoclase and the quartz plate became more water-wet using carbonated brine.
- The dynamic captive bubble technique gives us the ability to measure interfacial tension and contact angle in the same system, yielding values which are comparable to previously published data.
- The static bubble technique for measuring advancing and receding angle gave a larger range in measured contact angle (compared to the dynamic method) from the point of gas coming into first contact with the substrate up to the maximum base diameter measured using our experimental set up.

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