1. Introduction

[2] Interfacial phenomena upscale through the sediment porous network to define multiphase flow characteristics. Thus, interfacial phenomena control enhanced oil and gas recovery [Page and Baviere, 1991; Rosen et al., 2005], methane production from hydrate bearing sediments [Seo et al., 2002; Sun et al., 2004; Watanabe et al., 2005], and the ability to inject and store CO2 in geological formations [Chalbaud et al., 2009; Chiquet et al., 2007; Hildenbrand et al., 2004; Plug and Bruining, 2007; Suekane et al., 2009]. Temperature and pressure vary considerably in these natural systems: from cold and relatively shallow permafrost and marine sediments (e.g., Alaska north slope: ~7 MPa, 278K) to warm coal seams (e.g., Alabama Black Warrior Basin: ~7 MPa, 296K) and deep hot rocks onshore (e.g., Weyburn oil field: ~14 MPa, 323K). Therefore, CO2 can form a gas, liquid, or supercritical phase in various applications or environments.

[3] Interfacial tension arises at the molecular level as a result of van der Waals forces [Butt et al., 2006; Defay and Prigogine, 1966]. Three interfacial tensions can be identified in a liquid (l), fluid (f), and solid substrate (s) system (Figure 1). While fluid-liquid interfacial tension \( \sigma_{fl} \) is directly measurable, fluid-solid \( \sigma_{fs} \) and liquid-solid \( \sigma_{ls} \) interfacial tensions are assessed through indirect methods [Butt et al., 2006]. Foreign substances on the solid surface or within the fluids can modify any of the three interfacial tensions. The contact angle is influenced by other factors such as surface roughness, contact line fluctuations, vibrations, and viscous effects (see review by Decker et al. [1999]).

[4] The interfacial tension \( \sigma_{fl} \) between CO2 (“fluid” implies either gas or liquid) and liquid water is susceptible to changes in temperature and pressure. At ~298K, the interfacial tension decreases from ~72 to 25 mN/m as pressure increases from 0.1 to 6.4 MPa, and it reaches a constant value ~30 mN/m after CO2 liquefies (studies at 278–373K and up to 70 MPa can be found in the work of Chun and Wilkinson [1995], Dickson et al. [2006], Kvamme et al. [2007], Massoudi and King [1974a], and Sutjiadi-Sta et al. 2007]). Water salinity affects the interfacial tension between CO2 and brine [Chalbaud et al., 2009].

[5] The interfacial tension \( \sigma_{fs} \) between the solid substrate and CO2 decreases significantly with the increase in CO2 pressure for different substrates [Dickson et al., 2006; Sutjiadi-Sta et al., 2008]. For an increase in pressure (\( P = 0.1 \) to ~7 MPa), the corresponding decrease in \( \sigma_{fs} \) is 30 to ~0 mN/m in glass hydrophobized with dichlorodimethy-
dilane, 24 to \( \sim 0 \) mN/m in polytetrafluoroethylene (PTFE), and 80–17 mN/m in glass.

[6] On the other hand, the interfacial tensions between water and the solid substrate remains relatively stable with the increase in fluid pressure; for example, the water-PTFE interfacial tension remains at \( \sim 25 \) mN/m, for a pressure range between \( P = 0.1 \) and \( \sim 7 \) MPa [Dickson et al., 2006]. Ionic species may interact with the solid substrate and alter \( \sigma_{ls} \).

[7] The Young-Dupre equation relates the contact angle \( \theta \) to the mutual interfacial tensions: \( \cos \theta = (\sigma_{fl} - \sigma_{ls})/\sigma_{fl} \) (Figure 1). It follows that changes in interfacial tensions \( \sigma_{fl} \), \( \sigma_{ls} \), and \( \sigma_{fl} \) with \( \text{CO}_2 \) pressure alter the contact angle in water-\( \text{CO}_2 \)-substrate systems. For an increase in pressure from \( P = 0.1 \) to \( \sim 8 \) MPa, the increase in contact angle is \( \Delta \theta \approx 45^\circ \) on glass hydrophobized with dichlorodimethyldilane, \( \Delta \theta \approx 50^\circ \) on PTFE, \( \Delta \theta \approx 15^\circ \) on glass, \( \Delta \theta \approx 25^\circ \) on muscovite mica, and \( \Delta \theta \approx 60^\circ \) on coal [Chi et al., 1988; Chiquet et al., 2007; Dickson et al., 2006; Siemons et al., 2006; Sutjiadi-Sia et al., 2007].

[8] The purpose of this manuscript is to extend the scope of previous studies summarized above to include other substrates and pore fluid conditions that may be encountered in natural systems, particularly in the context of \( \text{CO}_2 \) geological storage. We place emphasis on the simultaneous determination of interfacial tension and contact angle. We note that, while there is extensive data on the solubility and diffusivity of \( \text{CO}_2 \) in water, there is very limited information on the diffusivity of water in \( \text{CO}_2 \); therefore, we include complementary tests to evaluate molecular diffusion. Finally, we use experimental results to assess \( \text{CO}_2 \) injectability and storage in geological formations.

2. Device and Materials–Test Procedure–Data Reduction

2.1. Apparatus

[9] We use the sessile droplet method to determine the evolution in interfacial tension \( \sigma_{fl} \) and contact angle. This test configuration allows us to explore the effect of relative density from gas \( \text{CO}_2 \) to liquid \( \text{CO}_2 \) conditions. Tests are conducted within a stainless steel, high-pressure chamber, internal volume \( \sim 55 \) cm\(^3\), which has a sapphire window to allow for optical measurements (Figure 2a). The cell is instrumented with a pressure transducer (OMEGA PX303-GV) and a thermocouple (copper-constantan, Conax Buffalo) placed in the vicinity of the droplet. A fiber optic port provides internal illumination. Separate injection ports are available for \( \text{CO}_2 \) and water. The water droplet sits on the selected substrate at the center of the cell (Figure 2b).

2.2. Materials

[10] Water droplets involve either deionized water or brine prepared by mixing water with natural halite crystals at room temperature and atmospheric pressure. The tested
Figure 3. A water droplet on PTFE substrate surrounded by CO2. (a) Changes in interfacial tension $\sigma_0$ and contact angle $\theta$ as CO2 pressure increases from 0.1 to 18.5 MPa. (b) Size reduction as water diffuses into the surrounding liquid CO2 (duration, ~400 min).

substrates include PTFE film, calcite crystal, clean glass (amorphous silica), and glass coated with oil (surface pre-treated with toluene and n-heptane and coated with oil of medium viscosity from Maracaibo Lake reservoirs, procedure in the work of Bryar and Knight [2003]).

2.3. Test Procedure

[11] The chamber is first subjected to vacuum and gradually flushed with CO2 (99.99% purity) to remove air. Then, we use a precision syringe to place a small water droplet (between 10 and 30 mm$^3$) on the horizontally resting substrate; such small droplets minimize gravitational effects and provide insight relevant to the scale of pendular water at interparticle contacts within sediments. The system is pressurized with CO2 in stages, from an initial pressure of 0.1 MPa to a maximum pressure of 20 MPa. Temperature remains within 296.5 ± 1.5K at all times. We record the evolution of the droplet geometry using high-resolution time-lapse photography (3 μm pixel size). Figure 3 shows a typical sequence of images gathered during pressurization and during water diffusion into liquid CO2. These images capture characteristic trends observed in most tests.

[12] We use images captured at stable temperature and pressure conditions to measure interfacial tension and contact angle, typically 8 min after each pressurization step. Although CO2 diffuses quickly into the water at the interface, chemical equilibrium is not guaranteed and chemical reactions such as CO2 speciation and calcite dissolution may continue during the test. Note that the water droplet consistently advances or recedes during pressurization.

2.4. Data Reduction: Interfacial Tension and Contact Angle

[13] Images are scaled and digitally processed to find the interface boundary using the Canny edge detection algorithm [Canny, 1986]. The CO2-water interfacial tension $\sigma_{fl}$, curvature radii $R_1$ and $R_2$, and the pressure jump $\Delta P$ at any point on the interface are related by Laplace’s equation [Blokhuis, 2004; Rotenberg et al., 1983],

$$\sigma_{fl} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P. \quad (1)$$

Gravity $g$ and the difference in density $\Delta \rho$ between water or brine and CO2 cause a pressure gradient $\Delta \rho g z$ along the droplet height. Let us consider cartesian coordinates $(x,z)$ measured from the droplet apex (see Figure 1c) and a parameterized representation of the interface based on the curve length $s$ (Figure 1d), then

$$\frac{dx}{ds} = \cos \phi \quad \text{and} \quad \frac{dz}{ds} = \sin \phi. \quad (2)$$

Since curvature radii are $1/R_1 = d\phi/ds$ and $R_2 = x/\sin \phi$, equation (1) can be rewritten as

$$\sigma_{fl} \left( \frac{d\phi}{ds} + \frac{\sin \phi}{x} \right) = 2\pi r_0 + \Delta \rho g z. \quad (3)$$

where $r_0$ is the curvature at the droplet apex. The recorded droplet profile permits recovering local values of $\phi$, $s$, $z$ everywhere and measuring $R_0$ at the apex. The difference in mass densities $\Delta \rho$ is computed from equations of state. For water density, we use expressions in the works of Perry and Green [1997] and McCutcheon et al. [1993]; we do not correct for minor changes in water density associated with CO2 dissolution. For CO2, we consider it as a pure phase and compute its density using the equation in the work of Duan and Sun [2003].

[14] The only remaining unknown in equation (3) is the interfacial tension $\sigma_{fl}$. We choose to simultaneously fit a large number of points $(x,z)$ to increase accuracy. We digitize the complete droplet profile (1000–6000 points) and fit the points with the lowest-degree polynomial that properly justifies the data; typically a degree 3–5 suffices. Contact angle $\theta$ (tangent when coordinates correspond to the substrate position), droplet volume, and surface area are calculated from the fitted polynomial assuming axisymmetry. Interfacial tension is obtained by minimizing the $L^2$ norm $E = \sum \varepsilon_i^2$ of individual errors in pressure $\varepsilon_i$ at each point along the droplet profile, where $\varepsilon_i$ is the difference between the pressure predicted with local curvatures $\sigma_{fl}(1/R_1 + 1/R_2)$ and the pressure as a function of depth $z$ from the apex $(2\pi r_0 + \Delta \rho g z)$. All calculations are repeated for both left and right halves of the droplet. This data-intensive measurement method gives consistent results, and the estimated error is $\Delta \sigma = \pm 2.5 \text{ mN/m}$ for interfacial tension and $\Delta \theta = \pm 0.6^\circ$ for contact angle.

2.5. Data Reduction: Diffusion

[15] Water diffuses into the surrounding CO2 until the two phases equilibrate. The instantaneous droplet volume and surface area allow us to evaluate the rate of water diffusion into the surrounding CO2 medium. The diffusion coefficient $D$ is inverted from successive forward simulations of the diffusion equation in terms of the concentration $c$ of water in liquid CO2, radial coordinates $r$, and time $t$,

$$\frac{dc}{dt} = D \left( \frac{2}{r} \frac{dc}{dr} + \frac{\partial^2 c}{\partial r^2} \right). \quad (4)$$

We estimate the droplet volume and initial droplet equivalent radius $R$ from the droplet shape. The injected liquid CO2 is water free, therefore $c(r > R, t = 0) = 0$. Even though the water droplet decreases in size, we assume that water dissolved in the space previously occupied by the con-
between CO₂ and water as a function of pressure; data conducted for each condition.

3. Results and Analyses

Table 1 shows tests conditions explored in this study. Experiments are designed to achieve high measurement precision and to improve invertibility of unknown parameters. In particular, interfacial tension cannot be properly resolved when the contact angle \( \theta \) is <80° and the droplet is flat, so emphasis is placed on nonwetting substrates when interfacial tension data are sought. The liquid CO₂ is pre-saturated with water to prevent water diffusion and to improve interfacial tension measurements in long duration tests. Experimental results and related analyses are presented next for the three parameters studied in this research: interfacial tension, contact angle, and water diffusion in liquid CO₂.

3.1. Interfacial Tension

Figure 4 shows the measured interfacial tension \( \sigma_{fl} \) between CO₂ and water as a function of pressure; data compiled from the literature are shown as well. Interfacial tension decreases as CO₂ pressure increases, and it remains constant once the CO₂ vapor-liquid boundary is reached (∼6.43 MPa at 298K). Three sets of experiments are identified:

1. Deionized water droplets (solid circles in Figure 4): Our results are in agreement with previous studies [Chun and Wilkinson, 1995; Kvamme et al., 2007; Massoudi and King, 1974a; Sutjiadi-Sia et al., 2007]. The interfacial tension between CO₂ and water \( \sigma_{fl} \) starts at ∼72 mN/m at 0.1 MPa and 295K and decreases linearly at a rate of ∼7 mN/m per MPa increase in CO₂ pressure until the liquid-vapor boundary is reached. Thereafter, the interfacial tension remains nearly constant at \( \sigma_{fl} = 20-30 \) mN/m. (Note: Kvamme et al. [2007] observed a smooth transition in the supercritical regime.)

2. Brine droplets (open diamonds in Figure 4): The interfacial tension \( \sigma_{fl} \) between CO₂ and brine is higher than between CO₂ and deionized water, and it exhibits lower sensitivity to pressure. (Note: higher pressure sensitivity has been observed in the supercritical regime at significantly higher temperatures [Chalbaut et al., 2009].)

3. Water droplets with organic compounds that dissolved from the substrate (crosses in Figure 4): The CO₂-water interfacial tension \( \sigma_{fl} \) is lower than for deionized water without organic contaminants, but rates of decrease with pressure are the same (in agreement with data from the work of Chun and Wilkinson [1995]).

Overall, values of CO₂-water interfacial tension can vary by ±10 mN/m, depending on the dissolved compounds in water.

These results are the consequence of molecular interaction taking place within the liquid and between water and the surrounding CO₂.

3.1.1. Interactions Within the Liquid

Foreign species modify the local electrical field within the liquid. Variations in interfacial tension \( \sigma (\text{mN/m}) \) with solute concentration \( c \) (mol/L) are anticipated in terms of surface excess of solute \( \Gamma (\text{mol·m}^{-2}) \) [Butt et al., 2006; Pegram and Record, 2007; Tuckermann, 2007],

\[
\frac{\partial \sigma}{\partial (\gamma c)} \bigg|_T = -\frac{RT}{\gamma c} \Gamma,
\]

where \( \gamma \) (dimensionless) is the solute activity coefficient and \( T \) (K) is temperature. In agreement with this theory, ions are depleted at the interface \( \Gamma < 0 \) in inorganic solutions, but there is enrichment of organic species \( \Gamma > 0 \) at the interface when organic compounds are present. In the case of CO₂, there is high concentration of dissolved CO₂ near the interface \( \Gamma > 0 \), causing the observed drop in interfacial tension [Chun and Wilkinson, 1995; Massoudi and King, 1974b; Sutjiadi-Sia et al., 2008]. Gibbs’ isotherms \( \Gamma = f (\gamma c) \) give insight into molecular mechanisms responsible for adsorption at the interface and differences among gases [Massoudi and King, 1974a]. Molecular dynamics simulations show the preferential alignment of water molecules near interface ions [Bhatt et al., 2004] and of water and CO₂.

Figure 4. Interfacial tension between water and CO₂. Lines indicate values reported in the literature for deionized water at ∼298K [a, Massoudi and King, 1974b; b, Chun and Wilkinson, 1995; c, Kvamme et al., 2007; d, Sutjiadi-Sia et al., 2007]. Note: the salt concentration in brine is ∼200 g (NaCl)/kg(water).
molecules at the interface [da Rocha et al., 2001; Kuznetsova and Kvimme, 2002; Kvimme et al., 2007].

3.1.2. Interaction With the Surrounding Fluid

[24] The proximity to and the number of near-neighbor charges in the surrounding fluid depends on the difference between fluid densities. Hence, higher interaction and lower interfacial tension are expected with increasing CO2 pressure and density, as suggested by the Suggen-Macleod equation \( \sigma = f(\Delta \rho) \) [Chalbaud et al., 2009; Chun and Wilkinson, 1995]. Consequently, the interaction with the external fluid and the value of \( \sigma_B \) remain relatively constant once the pressure exceeds the vapor-liquid boundary.

3.2. Contact Angle

[25] Figure 5 shows the evolution of contact angle \( \theta \) with pressure for all substrates. The following can be observed:

[26] 1. The contact angle on nonwetting PTFE substrates increases (from 100° to 140°), as pressure increases and remains almost constant after the pressure exceeds the liquid-vapor interface.

[27] 2. The contact angle on oil-wet silica increases slightly (from 85° to 90°) when CO2 pressure increases from 0.1 MPa to the pressure at the liquid-vapor boundary \( \approx 6.43 \text{ MPa at 298K} \); thus, this substrate can turn from slightly hydrophobic to hydrophobic upon pressurization. At any given pressure, contact angles are similar for brine and deionized water.

[28] 3. Contact angles on amorphous silica SiO2 and calcite CaCO3 substrates remain nearly constant with pressure. Dissolved NaCl in water increases the contact angle by \( \sim 20° \) for brine on SiO2 and \( \sim 4° \) for brine on CaCO3.

[29] 4. Published results for glass, PTFE, and coal substrates are similar to those obtained in this study [Chi et al., 1988; Dickson et al., 2006; Sutjadi-Sia et al., 2007].

[30] Our results also show that contact angles between (1) liquid-CO2 and water and (2) liquid-CO2 and all tested solid substrates (CaCO3, oil-wet SiO2, and PTFE) approach \( \theta \approx 0° \) in a vapor-CO2 atmosphere.

[31] Let us consider the Young-Dupré’s equation in a differential form to identify the influence that changes in each component exert on \( \cos \theta \) upon small changes in gas pressure,

\[
\frac{d(\cos \theta)}{dP} = -\frac{\sigma_{fl} - \sigma_{ls} \, \partial \sigma_{fl} / \partial P}{\sigma_{fl}} + \frac{1}{\sigma_{fl}} \frac{\partial \sigma_{ls}}{\partial P} - \frac{1}{\sigma_{fl}} \frac{\partial \sigma_{ls}}{\partial P}.
\]

This expression explains changes in contact angle reported in Figure 5:

[32] 1. On hydrophobic substrates (PTFE and oil-wet quartz): A reduction in \( \sigma_B = \sigma_{CO2-H2O} \) combines with a decrease in \( \sigma_{fl} = \sigma_{CO2-substrate} \) (reported in the literature) to cause an increase in contact angle with pressure.

[33] 2. On hydrophilic quartz and calcite: The addition of NaCl increases \( \sigma_B = \sigma_{CO2-H2O} \) and results in a higher contact angle. On the other hand, the decrease in \( \sigma_B = \sigma_{CO2-substrate} \) (not observed explicitly), and the contact angle remains relatively unchanged.

[34] The observed contact angle \( \theta \approx 0° \) for liquid CO2 substrate in vapor CO2 atmosphere is in agreement with the reported \( \sigma_{CO2(vapor)-CO2(liquid)} \approx 0 \).

3.3. Water Diffusion in Liquid CO2

[35] The decrease in droplet volume with time observed in Figure 3 was measured for several conditions. We inverted for the diffusion coefficient \( D \) of water in liquid CO2 using the procedure outlined earlier; results are summarized in Figure 6. The water solubility in liquid CO2 was assumed to vary from 1.05 kg/m3 at 10 MPa to 2.1 kg/m3 at 25 MPa (measurements at 298–303K [Chrustal, 1982; Jackson et al., 1995; Sabirzayov et al., 2002; Spycher et al., 2003; Wiebe, 1941]). Our measured values and previously reported data are plotted in Figure 7:

[36] 1. Previously published NMR experiments \( D = \) from 1.5 \times 10^{-8} to 2 \times 10^{-8} m^2/s at 298K, 13–20 MPa [Yu et al., 2003] and molecular simulations \( D = \) from 16 \times 10^{-8} to 2 \times 10^{-7} m^2/s at 308.9K, 6.3–17.1 MPa [Danten et al., 2005].

[37] 2. In our measurements, uncertainty in the solubility of water in CO2 is responsible for an estimation error of \( \varepsilon \approx \pm 4 \times 10^{-8} \text{ m}^2/\text{s} \).

[38] 3. Values range from \( D = 1.2 \times 10^{-7} \text{ to } 1.8 \times 10^{-7} \text{ m}^2/\text{s} \) for water to \( D = 1.0 \times 10^{-7} \text{ m}^2/\text{s} \) for brine. The lower diffusion coefficient for brine reflects the attraction of water to ions in the aqueous solution. In fact, we observe salt precipitation as water molecules leave the droplet and migrate into the bulk liquid CO2.

[39] 4. The measured diffusion of water in liquid CO2 is much faster than the diffusion of CO2 in water \( D = 2 \times 10^{-9} \text{ to } 5 \times 10^{-9} \text{ m}^2/\text{s} \) [Thomas and Adams, 1965], ions in water \( D \sim 10^{-9} \text{ m}^2/\text{s} \) [Sharma and Reddy, 2001], and
organic compounds in supercritical CO₂, \( D = 2 \times 10^{-8} - 1 \times 10^{-8} \text{ m}^2/\text{s} \) (experiments at 313K [Funazukuri et al., 1992; Liong et al., 1992; Sassiat et al., 1987]).

[40] A decrease in \( D \) with pressure is apparent.

[41] We corroborated our droplet-based results by means of a 1-D configuration using a capillary tube to create a steady state diffusion condition (data also shown in Figure 7). Values inverted from droplet tests are approximately twice higher from the 1-D steady state experiment \( D = 6.0 \times 10^{-8} \text{ m}^2/\text{s} \) (probably due to convective currents). Nevertheless, all our experiments confirm the very high diffusivity of water in liquid CO₂.

[42] The high diffusivity of water in liquid CO₂ is attributed to the small size of water molecules in terms of equivalent molecular radius and the low viscosity of liquid CO₂, \( \mu_{\text{CO₂}} \). Note: \( \mu_{\text{CO₂}} \) increases with pressure and decreases with temperature; values range from \( 2 \times 10^{-5} \text{ Pa} \cdot \text{s} \) at 5 MPa and 318K to \( 10^{-4} \text{ Pa} \cdot \text{s} \) at 30 MPa and 298K [Fenghour et al., 1998].

3.4. CO₂-H₂O-Substrate Chemical Reactions

[43] We witness mineral corrosion during these tests. Furthermore, we also observed the reprecipitation of calcite in the form of typical trigonal-rhomboic crystals on the mineral surface after water evaporation or water diffusion out of the droplet. SEM images are shown in Figure 8. Similar micron-size precipitated crystals are reported for calcite precipitation from calcium slurry [Montes-Hernandez et al., 2007]. Note: bicarbonate may precipitate as aragonite if temperature exceeds \( T > 303 \text{K} \) [Cowan and Weintritt, 1976].

[44] The presence of CO₂ changes the chemistry of the water droplet. Carbon dioxide dissolves in water with a solubility that depends on pressure and temperature (“aq” stands for aqueous form),

\[
\text{CO}_2(\text{g-or-l}) \leftrightarrow \text{CO}_2(\text{aq}),
\]

\[
\text{H}_2\text{O}(l) + \text{CO}_2(\text{aq}) \leftrightarrow \text{H}_2\text{CO}_3(\text{aq}) \text{ carbonic acid}.
\]
et al. Without CaCO₃ occur in the order of seconds for carbon hydration d[CO₂]/d
[65x89]32 0.0325 3.92 0.027 1.21 × 10⁻⁴ 0.03 s
6.4 1.376 3.09 1.14 8.14 × 10⁻⁴
10 1.421 3.07 1.18 8.14 × 10⁻⁴
20 1.559 3.05 1.29 8.83 × 10⁻⁴

4. Discussion: Implications to CO₂ Geological Storage

Carbonic acid ionizes stepwise to produce bicarbonate and carbonate ions,

\[ \text{H}_2\text{CO}_3(\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{HCO}_3^- (\text{aq}), \]

\[ \text{HCO}_3^- (\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{CO}_3^{2-} (\text{aq}). \]

Table 2 shows the concentration of these species at different pressures obtained from thermodynamic equations. The increase in CO₂ pressure results in both higher solubility of CO₂ and higher concentration of aqueous species. Reactions occur in the order of seconds for carbon hydration d[CO₂]/dₜ ~ 0.03 s⁻¹ [CO₂] (brackets mean concentration in mol/L) and it is even faster for stepwise ionization [Stumm and Morgan, 1996]. Therefore, the availability of species within the droplet is diffusion limited in real systems size \( L \) where the characteristic diffusion time is on the order of \( L^2/d \). [45] Calcite CaCO₃ experiences relatively fast reactions with water acidified by CO₂,

\[ \text{CaCO}_3(s) + \text{H}_2\text{O} + \text{CO}_2(g) \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-. \]

Dissolution rates are proportional to the pH difference with respect to the equilibrium condition, and aqueous species are produced proportionally to the CO₂ pressure increase [Drever, 1997]. Conversely, a reduction in CO₂ pressure produces nucleation of CO₂ in gaseous form and the precipitation of calcite. CaCO₃(s) buffering and dissolution causes a ~2 orders of magnitude increase in HCO₃⁻, as compared with the nonreactive case. Both chemical analyses of CaCO₃ dissolution and the estimated volume of precipitates in SEM images (thickness assumed ~0.3 μm) provide similar mass estimates.

4.1. CO₂ Injectability

The displacement of the saturating brine by liquid CO₂ depends on their viscosities \( \mu_{\text{CO}_2} \) and \( \mu_{\text{brine}} \), the pore flow velocity \( v \) and capillary resistance at pore throats. Let us consider a pore as a cylindrical tube length \( L \) going from node \( i \) to node \( j \). The equilibrium condition when liquid CO₂ displaces brine along the tube is given by

\[ P_i = P_j + 4 \frac{\sigma \cos \theta}{d} + \frac{32L}{d^2} (\mu_{\text{CO}_2} \mu_{\text{brine}} + \mu_{\text{brine}}), \]

where the second term is Laplace’s equation and the third term is Poiseuille’s equation. Therefore, wettability (e.g., \( \sigma \cos \theta > 0 \), if the host fluid is the wetting one) and viscous drag determine imbibition and the occupancy of pores by either the wetting or the nonwetting fluid. The balance between participating forces can be captured in two dimensionless ratios: between viscous components \( M \) and between viscous and capillary forces \( C \),

\[ M = \frac{\mu_{\text{CO}_2}}{\mu_{\text{brine}}} \quad \text{and} \quad C = \frac{\nu \mu_{\text{CO}_2}}{\sigma \cos \theta}. \]

Values of viscosity \( \mu_{\text{brine}} = (1 \pm 0.5) \times 10^{-3} \text{ Pa·s} \) at 323K and \( \mu_{\text{CO}_2} = (2\text{--}8) \times 10^{-3} \text{ Pa·s} \) at 318K and from 5 to 30 MPa [Fenghour et al., 1998; Netherton et al., 1977], readily show that the viscosity number is low for liquid CO₂–brine systems \( M = \mu_{\text{CO}_2}/\mu_{\text{brine}} \sim 10^{-2} \). On the other hand, the \( C \) ratio varies with distance to the injection well and pressure-dependent \( \sigma \) and \( \theta \) values.

[48] Different invasion patterns develop as a function of \( M \) and \( C \) [Lenormand et al., 1988; Pennell et al., 1996]. We can anticipate the following situations developing during liquid CO₂ injection into the reservoir:

[49] 1. Near the injection well, high flow velocity (high \( C \)-low \( M \)); Viscosity controls the invasion of CO₂ into the formation. Given the low viscosity number \( M \) for liquid CO₂–brine systems, liquid CO₂ will preferentially displace brine from the largest pores, but it will be prone to instability and viscous fingering may emerge [Lenormand et al., 1988].

[50] 2. Far from the injection well, low flow velocity (\( \nu \rightarrow 0 \), low \( C \); note that this condition applies as well at the interface against the seal layer during long-term quasi-static storage): Capillary forces control CO₂ invasion into the porous medium. Brine is the wetting phase and remains in the smaller pores. Capillary fingering may develop.

[51] Both viscous and capillary fingering patterns result in large irreducible saturation of the host fluid (brine). Oil–CO₂ phases behave differently to brine–CO₂ since part of the oil is miscible with CO₂ [Blunt et al., 1993].

4.2. Sealing Capacity of Geological Formations

The long-term storage of CO₂ is a quasi-static condition (\( \nu = 0 \), \( C = 0 \)) controlled by capillary forces at pore
the following analysis is conducted to identify the governing parameters and their interrelation.

1. Pore size distribution, mean value: Let us assume a lognormal distribution for pore size normalized by 1nm $x = \log(d/\text{nm})$ with mean $\mu_x = \text{mean}[\log(d/\text{nm})]$, standard deviation $\sigma_x$ = variance[log(d/\text{nm})] and probability density function,

$$\text{Prob}(x) = \frac{1}{\sigma_x \sqrt{2\pi}} \exp\left(-\frac{(x - \mu_x)^2}{2\sigma_x^2}\right).$$

The mean $\mu_x$ can be extracted from mercury intrusion porosimetry [Juang and Holtz, 1986] or estimated theoretically as a function of the void ratio $e$, the specific surface $S_e$, and the mineral density $\rho$. For conglomerates made of edge-to-face and face-to-face aggregations of clay particles (geometric factor $k$ between 6 and 12),

$$\mu_x = \log\left(\frac{k e}{S_e \rho \text{ nm}}\right).$$

2. Void ratio and compressibility: The void ratio depends on the effective stress $p'_f$ in agreement with Terzaghi’s consolidation theory [Burland, 1990; Terzaghi et al., 1996],

$$e = e_1 \text{ kPa} - C_e \log\frac{p'_f}{\text{1 kPa}},$$

where the void ratio $e_1 \text{ kPa}$ at $p'_f = 1 \text{ kPa}$ and the compressibility coefficient of the sediment $C_e$ increases with increasing surface.

3. Breakthrough pressure: For a given pore structure, there is breakthrough pressure $P^*_b$ determined by the pressure-dependent interfacial tension $\sigma$ and contact angle $\theta$,

$$P^*_b = \frac{4\pi \cos \theta}{d^*},$$

where the critical pore size $d^*$ is herein defined as the minimum pore size along a percolating path across the seal layer.

4. Critical pore size: The analysis of gas breakthrough experimental data from the works of Hildenbrand et al. [2002, 2004] and Horseman et al. [1999] indicates that $d^*/\text{nm} > 10^{-6}$; hence, the percolating path is made of pores all larger than the mean. The value of $d^*$ can be related to the mean $\mu_x$ by a factor $\alpha$ of the standard deviation $\sigma_x$,

$$\log\left(\frac{d^*}{\text{nm}}\right) = \mu_x + \alpha \sigma_x. \quad (13)$$

Data from the work of Horseman et al. [1999] are analyzed using this formulation to estimate $\alpha \sigma_x$. We compute $d^*$ from breakthrough (equation (12), water–helium interfacial properties from the work of Hough et al. [1952]) and $\mu_x$ from porosity (equation (10), mineral density and specific surface from the work of Rosborg and Pan [2008]). We obtain $\alpha \sigma_x = \log(d^*/\text{nm}) - \mu_x$. Results shown in Figure 9 indicate that $\alpha \sigma_x$ is relatively independent of effective stress, and it ranges between $0.7 \pm 0.15$ for this sediment (assumed geometric factor $k = 12$). Therefore, $d^*/\text{nm} = 10^{\mu_x + (0.7 \pm 0.15)}$.

5. Finally, we can express the breakthrough pressure for an immiscible fluid as a function of effective stress $p'$, sediment compressibility $(e_1 \text{ kPa}, C_e)$, pore structure $(S_e, \sigma_x, \alpha)$, and pressure-dependent interfacial tension $\sigma$ and contact angle $\theta$,

$$P^*_b = \psi \frac{S_e \rho \sigma \cos \theta}{e_1 \text{ kPa} - C_e \log\frac{p'_f}{\text{1 kPa}}} \quad (where \ 0.04 \leq \psi \leq 0.08),$$

where the factor $\psi = 4/(k(10^{\alpha \sigma_x}))$ groups theoretical and experimental constants and provides an order of magnitude estimation. Results in Figures 4 and 5 combine to make the wetting factor $\sigma \cos \theta$ a linearly decreasing function of pressure in either quartzitic and carbonate sediments, from $[\sigma \cos \theta] \approx 60 \text{ mN/m}$ at atmospheric pressure to $[\sigma \cos \theta] \approx 30 \text{ mN/m}$ on the L-V boundary. The wetting factor is very low for oil–wet sediments $[\sigma \cos \theta] < 5 \text{ mN/m}$, and capillary forces vanish. Spontaneous imbibition takes place when $[\sigma \cos \theta] < 0 \text{ mN/m}$. High values of breakthrough pressure are anticipated for clayey formations because of the high specific surface and small pore size; in this case, the presence of high-conductivity mesoscale features will define the geological plumbing and restrict storage capacity.

Other concerns regarding CO2 injection in geologic formations include change in surface charge of clays and associated double-layer effects due to decreased pore fluid pH [Palomino and Santamarina, 2005] and mineral dissolution and ensuing changes in effective stress leading to strain localization [Shin et al., 2008] and increase in permeability [Phillips, 1991].

5. Conclusions

Dissolved organic or inorganic species in water preferentially organize at the interface. Excess solute at the interface and the mass density of surrounding CO2 determine interfacial tension. In particular, the interfacial tension between water and CO2 decreases with pressure from $-65 \pm 14 \text{ mN/m}$ at atmospheric pressure to $-25 \pm 7 \text{ mN/m}$ beyond
the CO2 V–L boundary. The variability in each case reflects solute type and concentration.

[60] Contact angle \( \theta \) changes in agreement with Young-Dupré’s equation. On hydrophobic substrates, the increase in contact angle \( \theta \) with pressure can be as high as 60°. Oil-wet mineral surfaces may turn from hydrophilic at low gas pressure to hydrophobic at high gas pressure. There is a small decrease in contact angle on hydrophilic silica and calcite substrates.

[61] Water solubility in liquid CO2 cannot be neglected when interparticle pendular water is involved. The effective diffusivity of water in liquid CO2 is high \( D = 1.5 \pm 0.3 \times 10^{-7} \text{m}^2/\text{s} (D \sim 1.0 \times 10^{-7} \text{brine}) \) primarily due to the low viscosity of liquid CO2. This value is 2 orders of magnitude greater than diffusion values frequently invoked for ionic species in water.

[62] Pore water acidifies in the presence of CO2 and can react with mineral substrates. Calcrete dissolution, water diffusion in liquid CO2, and calcite reprecipitation can take place in short-time scales (i.e., days) for pendular water between contacts.

[63] Capillary pressure and viscous forces play an important role in determining CO2 injectability and the sealing capacity of geological formations. Two end-member scenarios can be identified: high-velocity viscosity-controlled flow (near injection wells) and quasi-static capillarity-controlled storage (far field and during long-term storage). Fingering and changes in imbibition patterns can develop.

[64] The breakthrough pressure is a function of sediment characteristics (primarily specific surface), overburden effective stress, and fluid pressure-dependent wetting conditions (interfacial tension and contact angle). The smallest pore size along a percolating path is larger than the mean pore diameter. It is anticipated that high-conductivity mesoscale paths will control the sealing capacity of clayey rocks.

Notation

\[ \sigma_f \] interfacial tension fluid–liquid, mN/m.
\[ \sigma_{s} \] interfacial tension fluid–solid, mN/m.
\[ \sigma_{g} \] interfacial tension liquid–solid, mN/m.
\[ P \] pressure, MPa.
\[ \theta \] contact angle, degrees.
\[ R_1, R_2 \] curvature radii, m.
\[ \rho \] density, kg/m³.
\[ x, z \] Cartesian coordinates, m.
\[ s \] curve length, m.
\[ \phi \] curve angle, rad.
\[ \varepsilon \] error.
\[ r \] radial coordinate, m.
\[ t \] time, s.
\[ D \] diffusion coefficient, m²/s.
\[ c \] solute concentration, mol/L, kg/M³.
\[ \Gamma \] surface excess of solute, mol/m².
\[ T \] temperature, K.
\[ \mu \] viscosity, Pa·s.
\[ v \] flow velocity, m/s.
\[ M \] ratio between viscous forces.
\[ C \] ratio between viscous and capillary forces.
\[ d \] pore size, m.
\[ x \] pore size normalized by 1nm.
\[ e \] void ratio.
\[ S_s \] specific surface, m²/kg.
\[ p' \] confinement, Pa.
\[ C_c \] compressibility coefficient of the sediment.
\[ p^* \] breakthrough pressure, Pa.

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