Pore-Scale and Conventional Wettability Measurement Considerations for Improving Certainty of Geological CO2 Sequestration

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PORE-SCALE AND CONVENTIONAL WETTABILITY MEASUREMENT CONSIDERATIONS FOR IMPROVING CERTAINTY OF GEOLOGICAL CO2 SEQUESTRATION

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Civil and Environmental Engineering

by

Mohammad Jafari
B.S., Bu-Ali Sina University, 2007
M.S., Bu-Ali Sina University, 2010
August 2018
to

My parents Ozra and Mohsen

and

My family
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Abstract

Parallel to the approach of developing zero-carbon-emission energies, other solutions have been recently proposed to decrease the amount of CO2 emissions into the atmosphere. Geological CO2 sequestration (GCS) has provided economic benefits and slight adverse environmental effects. GCS involves capturing CO2 from large producers, then injecting it into deep layers of the earth’s subsurface to be stored for hundreds to thousands of years. A safe and economic GCS requires a profound knowledge of immiscible CO2-water/brine fluid flow in CO2 storage sites including capillary pressure which has a barrier effect against leakage. The main uncertainty in measuring capillary pressure is due to the wettability, which is quantified by contact angle of water/brine interface on rock surface. The objective of this study is to explore the reasons of uncertainty observed in conventional contact angle measurement and introduce a more realistic pore level contact angle measurement.

The contact angle of water/brine on select minerals found in common rocks (silica and mica) was measured using a high-pressure, high-temperature chamber developed for a captive bubble test method. As an innovative method, pore-scale static and dynamic contact angles were also measured inside a high-pressure micromodel using a microscope. The results showed that the heterogeneity on minerals surface plays an important role in controlling contact angle variation with time. With unsaturated fluid (water/brine-CO2) condition, which is more realistic in the short-term after CO2 injection, the contact angle can increase due to a pinned triple line (the line on which the three phases of the liquid, gaseous, and solid surface meet) as a result of heterogeneity. An increased contact angle causes the capillary pressure to decrease resulting in a higher leakage risk. The micro-scale dynamic contact angle results showed that rocks were not as water-wet as assumed in literature when conventional measurement methods on flat surfaces of minerals were
used. An increase of pressure and salinity changed the glass (silica) behavior from water-wet to intermediate-wet. Pore-scale contact angle measurement provides more realistic wettability behavior of geo-materials and increases the certainty the simulations used for assessing safety and efficiency of storage sites.
Chapter 1. Introduction

1.1 Motivations

The population and the urban citizens have increased in the world (Fig. 1.1a). Growth energy demands with the sustained and rapid population growth have caused a swell in energy consumption (Fig. 1.1b) such as oil, coal, and natural gas, which result in more carbon dioxide (CO$_2$) emissions (Fig. 1.1c). Hence, an excessive amounts of emission into the atmosphere results in serious environmental problems such as temperature and sea level rise around the world (Fig. 1.1d, Rohrer, 2007).

Figure 1.1. World population (a), CO$_2$ emission (b), Energy consumption (c), Temperature and sea level change (d) since 1800 year [Fragaszy et al., 2011; De Silva et al., 2015]

The most CO₂ emissions come from energy production consumption (42%) in the world (Fig. 1.2a). Also, both industry and road transport have influenced the significant amount of CO₂ emission (Fig. 1.2a).

Figure 1.2. CO₂ emission by different sectors and countries in the world, a) CO₂ emissions by sector in the world, b) Energy-related CO₂ emissions by country, c) CO₂ emissions from fossil-fuel use and cement production in the top 6 emitting countries, d) China leads the world in yearly carbon emissions (International Energy Agency, 2006; International Energy Agency, 2013).

To reduce CO₂ emission, International Energy Agency (IEA)-World Energy has released the New Policy Scenario (IEA, 2015), which includes (1) the decrease in demands for energy services such as lighting or transport services, and (2) the switch from coal to gas consumption. It is expected that 3.1 Gt and 15.0 Gt of CO₂ will be reduced until 2020 and 2025 with the new policy, respectively (Fig. 1.3).
Furthermore, a couple of scenarios have been suggested such as: employing energy efficiency and conservation practices, using carbon-free or reduced-carbon energy resources, and capturing and storing carbon from fossil fuels or the atmosphere [International Energy Agency, 2015]. Among these options, carbon capture and storage (CCS) is expected to reduce CO₂ emission from the atmosphere dramatically [Singh et al., 2015; Van Ruijven et al., 2016]. CCS is the process of capturing and separating of CO₂ from the atmosphere or industry emission sites and storing it in different forms. If the storage place is underground rock formations, it is called geological CO₂ sequestration (GCS) including three processes of capturing and compressing the CO₂, transporting to the storage site, and injecting underground stratifications for long-term storage [Holloway, 2005, 2007]. Geological CO₂ sequestration (GCS) is considered as a promising method to control CO₂ emission for a long time in large scale [Bachu, 2000a; Holloway, 2005; Bachu et al., 2007; Holloway et al., 2007; Godec et al., 2011].
Global CCS Institute defines a large scale CCS project involving capture, transport, and storage of CO\textsubscript{2} more than 800,000 tones yearly for coal-based power plants and more than 400,000 tones for other projects [Global CCS Institute, 2015]. The main idea of GCS is to trap CO\textsubscript{2} into deep sites for hundreds to thousands of years in a safe condition. Depleted oil and gas reservoirs, saline aquifers, deep coal seams, and deep ocean sediments are the main candidates as CO\textsubscript{2} storage sites [Bachu, 2000a; Pashin and McIntyre, 2003; Massarotto et al., 2010; Tang et al., 2014].

1.2 Scope and Purpose of the Study

The main objective of this research study is to increase the knowledge of geological CO\textsubscript{2} sequestration as a promising method to mitigate anthropogenic CO\textsubscript{2} emissions. Two main goals are pursued in such projects: (1) economic purposes including how ease we can inject CO\textsubscript{2} into the storage sites and how efficient CO\textsubscript{2} can sweep water out of the rocks pores to increase storage capacity; (2) safety of the storage site which includes the leakage preventing by sealing rock and immobilizing CO\textsubscript{2} inside rock pores. For both goals, one needs to find the preference of water and CO\textsubscript{2} for sticking to rock surface (which is determined by contact angle between water/CO\textsubscript{2}/rock), since it governs the fluids flow properties in the porous medium of the storage rock layers.

The present research includes two main parts: the first part consists of conventional experimental studies of common minerals (i.e., silica and mica) in laboratory, and the second part includes pore-scale wettability studies of the two-phase immiscible fluid flow and assessing the pressure and salinity effect on pore-scale dynamic contact angle measurements. The primary goals of the present study can be categorized as below:

- Investigation of the wettability behavior of the rock minerals at geological CO\textsubscript{2} sequestration condition (i.e., elevated pressure and temperature).
• Exploring the potential reasons of uncertainty and discrepancy observed in literature for experimental observations.

• Decreasing the short-term leakage probability of the CO₂ storage site.

• Pore-scale wettability behavior of geo-materials considering the size effect on contact angle measurement.

1.3 References:


Chapter 2. Literature Review

2.1 Possible GCS Sites

Figure 2.1 shows different CO₂ phases in different range of pressure and temperature, which present that CO₂ exists as a supercritical state at a temperature higher than 31.1° C and at a pressure higher than 7.38 MPa. At this condition, CO₂ behaves similar to a gas to fill the entire accessible pores, but its density is similar to a liquid, which causes CO₂ storage efficiency to increase due to higher density of CO₂ [Bachu, 2003]. Such favorable condition for CO₂ storage usually requires the depths more than 800 m considering a typical geothermal gradient around 25° C/km and hydrostatic pressure [Holloway and Savage, 1993].

![Figure 2.1. Carbon Dioxide: Temperature-Pressure Diagram](Copyright © 1999 ChemicaLogic Corporation, 99 South Bedford Street, Suite 207, Burlington, MA 01803 USA. All rights reserved).

However, safety concerns usually limit using very deep storage sites (i.e. ~2000 m) for CO₂ sequestration due to high pressure demanded. Moreover, density of CO₂ does not increase considerably for such deep depth anymore, so injection is not cost-effective (For detail in CO₂ density and viscosity change with pressure and temperature please refer to Bachu and Adams, 2003; Nordbotten et al., 2005). Thus, storage sites located between 800 m and 2000 m depth are the most favorable case, which have the ranges of temperature from 30° C to 60° C, and pressure from 7.8 MPa to 19.6 MPa based on the assumption of 10° C temperature at surface, a thermal gradient of 25° C/km, and a hydrostatic pressure. Also, other technical considerations such as capacity, efficiency, and safety are required for a site selection, which are discussed in this section. Possible geological sites for GCS projects are following:

2.1.1 Deep Depleted Oil or Gas Reservoirs

In the primary production of oil, the natural high pressure of formation is used for possible GCS sites. After the loss of pressure, the secondary production of oil is achieved by the injection of water called water-flooding. For tertiary production, other fluids such as water steam, CO₂, CO₂ foam, nitrogen, flue gas, gel, and polymer are required to modify residual oil properties and enhanced oil recovery (EOR) [Dong and Huang, 2001; Tore et al., 2002; Wo et al., 2009; Manrique et al., 2010; Al-ali et al., 2013]. After final oil production, oil-fields are left as depleted oil reservoirs due to the low efficiency in production with long time and high costs consumption.

However, depleted oil reservoirs are very attractive for CO₂ storage because of the existence of a sealed layer on the top of the oil-field, pre-existing wells ready for CO₂ injection, and available necessary facilities as well as the long-time well-established technology of CO₂ injection into reservoirs. Moreover, relatively small differences in density and viscosity between injected CO₂
and hydrocarbon fluids cause less segregation of two fluids, which makes the lower possibility for CO₂ accumulation under the caprock when comparing CO₂ storage in saline aquifers [Bachu, 2000a; Al-Abri and Amin, 2010]. In addition, depleted reservoirs already have trapped oil and gas for millions of years, which could guarantee the safety of CO₂ storage although recently some concerns have been raised. [Note that more explanation will be provided in the part 3.1 for this problem (Structural trapping mechanism)].

In spite of the advantages mentioned above, depleted oil/gas reservoirs have lower storage capacity (i.e., world estimation at 675–900 Gt of CO₂) than deep saline aquifers (world estimation at 1,000-10,000 Gt of CO₂) [IPCC, 2005]. Besides, more residual oil or gas in reservoirs can be produced with developing technologies in the future [Bachu, 2000a].

It implies that the efficiency of CO₂ injection is very high and deep depleted oil is one of favorable potential sites as CO₂ storages regardless of its small-volume capacity (i.e., world estimation at 675–900 Gt of CO₂) in relation to other sites [IPCC, 2005].

2.1.2 Unminable Coal Seams

Unminable coal seams are the thin layer of coal seams placed in very deep earth formations. Since coal production from unminable coal beds is not efficient, it has been considered for long-term CO₂ sequestration [Pashin and McIntyre, 2003; Massarotto et al., 2010]. The storage capacity and safety depend on their dimensions and depth, coal properties, flow characteristics, amount of existing methane, volume and type of hydrocarbons, and basin topography and hydrology [Li et al., 2013b]. Injection of CO₂ into coal seams has the advantage of producing methane as well as entrapping CO₂ with higher sorption selectivity of CO₂ than methane (one methane molecule is replaced with two CO₂ molecules), which is called CO₂-ECBM (enhanced coalbed methane
recovery using CO$_2$) [Gunter et al., 1997a]. However, the adsorption of CO$_2$ in coal seams results in coal swelling that causes the decrease in both permeability and injectivity [Cui et al., 2007].

Unminable coal seams are expected to store 3 Gt - 200 Gt of CO$_2$ in the world and primarily located near CO$_2$ emission points [IPCC, 2005]. The utilization of unminable coal seams as a CO$_2$ storage depends on the facility like pipeline network, permeability in the field, and sealing capacity.

2.1.3 Hydrate-Bearing Sediments

Methane hydrates are formed with methane (CH$_4$) and water at quite a low-temperature and high-pressure conditions. For example, when temperature is 273.15K, pressure should be higher than 2.5MPa to form hydrate [Jung et al., 2010]. Methane hydrate is found in marine continental margin and permafrost sediments, and is called as hydrate-bearing in sediments. Methane hydrate is a potential energy source due to the massive amount of reserves that is estimated about 500-10,000 Gt of carbon [Kvenvolden, 1988; Collett, 2002; Ruppel and Pohlman, 2008]. Methane can be recovered from hydrate-bearing sediments by depressurization, heating, or chemical injection. Especially CO$_2$ injection into hydrate-bearing sediments can produce CH$_4$, and entrap CO$_2$ as forming CO$_2$ hydrate at the same time [Ota et al., 2005a; McGrail et al., 2007; Zhou et al., 2008; Howard et al., 2012]. This process of CH$_4$-CO$_2$ exchange or CH$_4$-CO$_2$ replacement, makes hydrates bearing sediments a potential CO$_2$ storage site.

The extent of CH$_4$-CO$_2$ replacement and its efficiency is affected by pressure- and temperature-dependent solubility, interfacial properties, relative viscosity, permeability, density between water and CO$_2$, invasion patterns and specific surface of the hydrate phase, fluid expansion after replacement, and changes in effective stress [Jung et al., 2010].
As the main trapping mechanism in hydrate-bearing sediments is the replacement of methane with CO₂, most of the previous studies focused on replacement efficiency. Experimental results indicated that CH₄-CO₂ replacement rate increases with raising CO₂ gas pressure and gains near the CH₄ hydrate phase boundary. However, when CO₂ liquefies, CH₄-CO₂ replacement rate remains relatively constant [Ota et al., 2005a, 2005b; Mcgrail et al., 2007]. The replacement ratio increases when a mixture of CO₂ and N₂ is used for exchange due to the smaller N₂ molecule size [Park et al., 2006]. CH₄-CO₂ replacement occurs locally and gradually, so that the overall hydrate mass remains solid [Jung et al., 2010]. One of the main concerns in methane production is the instability of such sediments due to methane extraction, but experimental results successively showed by replacement of CO₂, no significant change in global stiffness happens for CH₄ hydrate-bearing sediments with hydrate saturation around 5 to 10% [Espinoza and Santamaria, 2011]. While previous studies show that CH₄-CO₂ replacement in methane hydrate is favorable, and the sediments can keep the stability during the replacement, more studies are needed considering the lower replacement rate and the limited capacity of hydrate-bearing sediments for CO₂ storage [Jung et al., 2010].

2.1.4 Deep Saline Aquifers

Deep saline aquifers contain entrapped fossil water between deep sealed layers, which is not considered for drinking purpose or agriculture activities due to a high concentration of dissolved salts (i.e., salinity is mostly higher that 35000 ppm) [Koide et al., 1995; Weir et al., 1995; Longworth et al., 1996]. Saline aquifers have been considered as sites with the highest potential for CO₂ storage because of their enormous capacity of roughly 1,000 to 10,000 Gt of CO₂, which is 99% of possible storage capacity in the world [White et al., 2003; IPCC, 2005; Michael et al., 2010]. Though the capacity estimation of saline aquifers has a significant uncertainty due to
different assumptions for basins volume, porosity, chemical properties of formations, CO₂ density, and technology limitation, saline aquifers have been considered as sites with enough storage capacity for predicted CO₂ emission rate for hundreds or thousands of years [Bruant et al., 2002].

In this research, technical issues of CO₂ storage in deep saline aquifers are more emphasized than other storage sites because of high capacity and potential.

2.2 Trapping Mechanisms in Saline Aquifers

While the standards for target time of a sequestration project has not clear yet, a growing consensus shows that a long period of safe storage is highly needed [Benson and Cole, 2008b]. For example, Hepple and Benson, (2005) suggested that over one thousands of year, storage site should retain 90 to 99% of injected CO₂. To ensure the retention capability of a storage site, a comprehensive knowledge of trapping mechanisms is necessary. In this section, four main trapping mechanisms in saline aquifers will be explained for geological CO₂ sequestration.

2.2.1 Structural Trapping

Injected CO₂ in saline aquifers or depleted oil and gas reservoirs has lower density rather than resident brine. Also, a long time period (couple of hundred years) is required to dissolve high portion of the injected CO₂ into the brine or the oil existing in the reservoir comparing with the injection period (a few years or decades). Thus, the injected CO₂ will rise buoyantly and accumulate beneath the caprock. Lower permeability (i.e., 1×10⁻⁵ to 2.1×10⁻¹ millidarcy (Hou et al., 2012)) and higher capillary pressure of the caprock can resist against the buoyancy force of CO₂, which causes an increase of uplift pressure on the caprock. Structural failure of the caprock results in removing the impermeable barrier and leakage of CO₂ occurs. Thus, storage safety
depends on the caprock’s ability to trap CO\textsubscript{2} for a long time within a range of several hundreds to thousands of years [IPCC, 2005; Chiquet et al., 2007a].

CO\textsubscript{2} leakage through the caprock may occur in the two following ways: (1) long-term capillary breakthrough of CO\textsubscript{2} by capillary sealing efficiency [Hildenbrand et al., 2004; Al-Bazali and Zhang, 2005; Chiquet et al., 2005] and (2) hydraulic or thermal fracturing of the caprock by the pressure buildup and temperature decrease resulting from the CO\textsubscript{2} injection [Chiquet et al., 2007a].

Long-term capillary breakthrough of CO\textsubscript{2} is related to capillary pressure in the caprock. Figure 2.2 shows a pore throat and a curved interface between wetting (brine) and nonwetting (CO\textsubscript{2}) phases in the caprock. Capillary pressure, which is defined as pressure difference between brine and CO\textsubscript{2} phases, is calculated as follows:

\[ P_{c, CO_2} = P_{CO_2} - P_w = \frac{2 \gamma_{w, CO_2} \cos \theta}{R} \]  

(2-1)

Where \( P_w \) is the pressure in the brine phase, \( P_{CO_2} \) is the injected CO\textsubscript{2} pressure, \( R \) is an effective pore radius, \( \gamma_{w, CO_2} \) the brine-CO\textsubscript{2} interfacial tension (IFT), and \( \theta \) is the contact angle of the mineral/brine/CO\textsubscript{2} system (Fig. 2.2). \( P_{c, CO_2} \) is the capillary pressure across the CO\textsubscript{2}-brine meniscus in a pore throat, which prevents the penetration of CO\textsubscript{2} into the caprock. When the pressure difference between CO\textsubscript{2} and brine exceeds the capillary pressure at the caprock, CO\textsubscript{2} will advance along the channel and consequently a slow Darcy flow will occur [Robert R. Berg, 1975; Tim T. Schowalter, 1979; Dullien, 1992; Hildenbrand et al., 2002; Li et al., 2005].

The capillary-sealing efficiency depends on the brine-CO\textsubscript{2} interfacial tension (IFT) and the contact angle in the caprock conditions. Recent studies show that water-CO\textsubscript{2} IFT values are within the range of 20–35 mN/m for pressures in the range of 6–20 MPa and temperatures below 71°C [Hildenbrand et al., 2004; Bachu and Bennion, 2009; Bachu and Brant Bennion, 2009; Chalbaud et al., 2009; Georgiadis et al., 2010], which increase a little with the salinity in the water [Massoudi
and King, 1975]. Also, a recent study reported that the increase in the contact angle is 17.6° ± 2.1°, with the increased pressure from 0.1 MPa to 25 MPa, and the increase of the contact angle is 19.6° ± 2.1° with the increased salinity from 0 to 5 molarity [Jung and Wan, 2012]. Thus, as the breakthrough pressure of CO₂ varies in proportion to the IFT and contact angle, the sealing capacity of a given caprock with respect to CO₂ is much lower than with the respect to hydrocarbons [Li et al., 2006]. Hence, a sealing layer that have retained hydrocarbons for millions of years may not a guarantee for retaining CO₂.

![Diagram of CO₂ injection into saline aquifers](image)

**Figure 2.2.** Contact angle and interfacial tension during CO₂ injection into saline aquifers containing brine [Tokunaga et al., 2011]
The increased pressure in saline aquifers influence the underground balanced forces, which causes the risk of reactivation of nearby faults to increase. Moreover, the excessive pressure by CO\(_2\) injection causes migration of fluids, which can penetrate between faults and decrease the friction between them [Cappa and Rutqvist, 2011]. Finally, hydraulic or thermal fracturing of the caprock can occur during/after CO\(_2\) injection into geological storage, which should be considered when the vast number of faults and the high risk of earthquakes exist. The large-scale injection of CO\(_2\) in brittle rocks usually found in interior continents sites could trigger seismic activity in pre-existing faults. Also, an earthquake from a tectonical activity can jeopardize the seal integrity of storage sites [Zoback and Gorelick, 2012].

### 2.2.2 Capillary Residual Trapping

Capillary trapping is a result of the consequence of hysteresis by drainage and imbibition process during/after CO\(_2\) injection in the porous medium. CO\(_2\) injection in saline aquifers generates a drainage process, which displaces the resident brine with injected CO\(_2\) in the pores. After CO\(_2\) injection completes, the brine returns to the storage site, which generates an imbibition process and causes some amounts of CO\(_2\) to be trapped by capillary pressure [Juanes et al., 2006; Bal et al., 2015]. Thus, the increase of CO\(_2\)-brine displacement efficiency and capillary pressure causes the greater chance of capillary trapping [Chatzis and Morrow, 1984; Morrow et al., 1988; Lake, 1989; Blunt and Scher, 1995; Ding et al., 2001; Ding and Kantzas, 2007; Cense and Berg, 2009]. Capillary pressure can be estimated using the equation 2-1 consisting of pore radius, interfacial tension, and contact angle. Higher capillary residual trapping capacity is anticipated when contact angle is low (or the system is water-wet) because the trapping CO\(_2\) cannot migrate due to high capillary pressure (Eqn. 2-1) [Amott, 1958; Blunt and Scher, 1995]. While a CO\(_2\)-wet system has a very lower capillary trapping capacity rather than water-wet system, such system is
very rarely found in saline aquifers \cite{Pentland et al., 2011}. The CO$_2$-brine displacement efficiency is influenced by a couple of parameters such as CO$_2$-, and brine-viscosity, contact angle, interfacial tension, and injected CO$_2$ velocity which will be explained in section 4.2 in detail.

Less CO$_2$ migration in pores is anticipated at higher capillary trapping, which contributes to solubility- and mineral- trapping mechanisms; the disconnected bubbles of CO$_2$ surrounded by brine have a large surface to volume ratio, which increases dissolution rate. Furthermore, highly distributed CO$_2$ bubbles in pores of a large volume of the reservoir cause both CO$_2$-mineral reaction and the precipitation to increase \cite{Wildenschild et al., 2011; Akbarabadi and Piri, 2014}. It implies that higher safety in the sites with residual trapping capacity can be anticipated due to additional solubility- and mineral- trapping effects.

### 2.2.3 Solubility Trapping

The CO$_2$ solubility in water raises by the increase in pressure and the decrease in temperature has been reported in previous studies \cite{Holloway and Savage, 1993; Koide et al., 1993; Bachu, 2000b; Ennis, J.; Paterson, 2000}. Higher CO$_2$ solubility relevant to high pressure- and high temperature conditions in GCS sites causes a long-term sequestrating mechanism during hundreds of years that is defined as a solubility trapping.

A couple of processing and parameters such as molecular diffusion of CO$_2$, convection of CO$_2$ dissolved brine, and chemical composition in brine and formation rock influence on the increased CO$_2$ dissolution into brine \cite{Garc, 2001; Ennis-King and Paterson, 2005; Portier and Rochelle, 2005; RIAZ et al., 2006; Xu et al., 2006; Han and McPherson, 2009; Li et al., 2013a}. Molecular diffusion defined as the migration of molecules from higher- to lower-concentration regions, results in continuous CO$_2$ dissolution in brine until reaching the solubility. Also, injected CO$_2$ in saline aquifers moves under the caprock due it its lower density than brine and dissolves into the
brine, which causes the density of brine to increase under the caprock (2-3% higher density than CO$_2$-free brine). Thus, the CO$_2$-rich brine with higher density below the caprock migrates to CO$_2$-free brine zone, and mixes with it by the convection between CO$_2$-rich brine and CO$_2$-free brine, which results in more CO$_2$ dissolution in saline aquifers [Garc, 2001; Ennis-King and Paterson, 2005; RIAZ et al., 2006; Xu et al., 2006; Han and McPherson, 2009; Li et al., 2013a]. Diffusion and convention requires a long-term period. Thus, the solubility trapping in GCS has been considered as a long-term sequestrating mechanism during hundreds of years. Studies show that structural and capillary trapping govern the sequestration mechanism in a short period, but solubility trapping has a significant portion of CO$_2$ sequestration mechanism according to time [Zhang et al., 2009].

2.2.4 Mineral Trapping

The dissolved CO$_2$ in brine chemically reacts with cations that are present in the water of saline aquifers or from dissolved minerals of rock formation, and precipitates. This mechanism is called as mineral trapping for permanent CO$_2$ sequestration because the reacted CO$_2$ is immobilized in the pores by the precipitation [Bachu et al., 1994; Perkins, E. H., Gunter, 1995; De Silva et al., 2015]. Previous studies show that substantial mineral trapping takes place within 6-40 years after injection but it continues for hundreds of year [Gunter et al., 1997a].

Dissolved CO$_2$ in brine generates the carbonated acidic condition in saline aquifers, which results in the dissolution of the rock formation and cations availability in the water. The following equations explain the chemical reaction happened during CO$_2$ dissolution [De Silva et al., 2015]:

\[
CO_2 (\text{gas}) \rightarrow CO_2 (\text{aqueous})
\]

\[
CO_2 (\text{gas}) + H_2O (\text{liquid}) \leftrightarrow H_2CO_3 (\text{aqueous})
\]

\[
H_2CO_3 (\text{aqueous}) \leftrightarrow H^+ (\text{aqueous}) + HCO_3^- (\text{aqueous})
\]
\[ HCO_3^- (\text{aqueous}) \leftrightarrow H^+ (\text{aqueous}) + CO_3^{2-} (\text{aqueous}) \] (2-2)

Equation 2-3 presents that the dissolution of CO\(_2\) in water causes the lower water pH, which dissolves more minerals in rock formation. The bicarbonate reacts with the cations, which results in the precipitation of several minerals such as calcite, magnesite, and siderite (Eqn. 2-3) [Gunter et al., 1997b; Ortoleva et al., 1998]

\[
\begin{align*}
HCO_3^- + Ca^{2+} &= CaCO_3 + H^+ \\
HCO_3^- + Mg^{2+} &= MgCO_3 + H^+ \\
HCO_3^- + Fe^{2+} &= FeCO_3 + H^+ 
\end{align*}
\] (2-3)

A storage site with low salinity and existence of the rocks containing calcium and magnesium is expected for immobilization of CO\(_2\) by mineral trapping [Bachu et al., 1994]. Brine absorbs less CO\(_2\) than brackish water because of the salting out effect. Geochemical reactions in a carbonate unit may cause an increase of dissolved CO\(_2\) by 1-4% depending upon formation water chemistry [Bachu et al., 1994; Benson and Cole, 2008b]. Furthermore, CO\(_2\) solubility decreases with rising salinity [Wiebe and Gaddy, 1939; Duan and Sun, 2003; Duan et al., 2006; Sasaki et al., 2014].

An aquifers including shale, sandstone, carbonate, basalt, volcanic debris, and aluminum-silicate minerals have high mineral trapping capacity for CO\(_2\) injection [Lagneau et al., 2005; Bachu and Bennion, 2008; Izgec et al., 2008; Gislason et al., 2010; Zhou et al., 2014].
2.3 Important Issues for Saline Aquifers as GCS Storage Site

2.3.1 CO2 Injectivity

One of the main objective of any storage project is to inject CO2 with the highest possible rate to decrease the costs by minimizing the project time, number of wells, and infrastructures costs [Burton et al., 2009; Zhang et al., 2013]. Injectivity is the easiness of injecting a fluid into a geological formation and defined by ratio of the injection rate to the pressure difference between the well and the formation. Using Darcy’s law, the volumetric injectivity is explained by the below equation [Xie et al., 2015]:

\[ J = \frac{q}{\Delta P} = \frac{2\pi kh}{\mu \ln(0.472r_e/r_w)} \]  (2-4)

Where \( J \) is volumetric injectivity; \( q \) is volumetric injection flow rate; \( \Delta P \) is pressure difference between the well and the formation; \( k \) is the permeability of the formation; \( h \) is the formation thickness; \( \mu \) is the viscosity of the injected fluid which is the viscosity of CO2 in GCS; \( r_e \) is equivalent (or effective) formation radius and \( r_w \) is injecting well radius.

Injectivity depends on properties of a formation and well such as length of injecting well screen or effective formation thickness, vertical and horizontal permeability of formation, porosity of formation, fracture pressure, heterogeneity, and fluid properties like viscosity. These parameters may vary from different sites or even may change in different areas and depths of a formation, so pilot and demonstration tests for a specific place is necessary to ensure an acceptable injectivity [Wei et al., 2013; Xie et al., 2015].

Increasing injection pressure can results in increase of injection rate. However, buildup pressure critically affects the increased mechanical stress and deformation in the formation and injection region, which consequently could cause microseismicity, faults reactivation,
fractures development, and ground surface uplift [Rutqvist et al., 2007; Ferronato et al., 2010; Cappa and Rutqvist, 2011; Zhu et al., 2015]. Generally, the lower permeability in the formation requires more number of injecting wellbores or results in hydraulic fracturing [Jikich et al., 2003; Zhang et al., 2013]. While hydraulic fracturing has been used in shale or other tight formation to increase injectivity and gas production with the increased permeability, GCS has a conflict with hydraulic fracturing since the main concern is integrity of sealing caprock [Elliot and Celia, 2012].

2.3.2 CO\textsubscript{2}-brine Displacement Efficiency in Saline Aquifers

A higher injectivity as well as a horizontal and vertical sweep efficiency are crucial to ensure the capacity of a storage site for a successful and economic geological CO\textsubscript{2} sequestration project. The CO\textsubscript{2}-brine displacement efficiency (or storage efficiency) is defined as the stored CO\textsubscript{2} in an aquifer over the maximum possible amount of CO\textsubscript{2} in saline aquifers [van der Meer, 1995; Okwen et al., 2010]. For enhanced oil recovery purposes, closer density of the supercritical CO\textsubscript{2} (scCO\textsubscript{2}) to light oils in comparison with other gases like methane makes CO\textsubscript{2} a proper injecting fluid due to decreasing gravity segregation. In addition, CO\textsubscript{2} has higher viscosity in comparison with other gases like methane, which reduces the sweep efficiency problems in enhanced oil recovery [Please refer to Oldenburg et al., (2001) for comparing density and viscosity of CO\textsubscript{2} and methane in different pressures]. However, when CO\textsubscript{2} is injected into saline aquifers, low CO\textsubscript{2}-brine displacement efficiency is anticipated due to lower density and viscosity than brine, which cause injected CO\textsubscript{2} to be segregated by gravity and to migrate upward as well as fingering (for details of CO\textsubscript{2} density and viscosity in different pressures and temperatures, please refer to Bachu (2003) and Nordbotten et al. (2005)). Thus, the sweep efficiency in vertical direction decreases [Nordbotten et al., 2005], and the entire porous media cannot be swept in horizontal direction due to fingering [Please note fingering will be explained in detail later in this section]. Therefore,
estimation of the total pore volume of a formation does not guarantee the fraction of available pore volume that can be occupied by the injected CO$_2$ [Bachu et al., 2007].

The period of injection and displacement of brine by CO$_2$ is very short comparing to the long-term process of CO$_2$ solution in brine [Please note that short- and long-term period were already introduced in structural trapping]. Also, displacement of the brine in saline aquifers by CO$_2$ can be assumed by an immiscible displacement considering the typical thermodynamic of reservoirs (Pressure = 10–70 MPa, Temperature = 40–120 °C), which has been well-understood in pore scale [Kazemifar et al., 2016]. Different displacement patterns are formed based on the balance between the dominant forces in a two dimensional displacement including viscous, capillary, and gravity (or buoyancy) forces. Lenormand et al. (1988) proposed two dimensionless numbers such as capillary number and viscosity ratio to characterize the fluid displacement regime in a horizontal direction by neglecting the buoyancy effect (gravity effect). Capillary number shows the competition between viscous forces of injected CO$_2$ and capillary pressure force between injected CO$_2$ and defending water, and is defined as:

$$Ca = \frac{V\mu_{CO_2}}{\gamma \cos \theta}$$  \hspace{1cm} (2-5)

where, $V$ is the bulk velocity of injected CO$_2$ (or Darcy velocity), $\mu$ the CO$_2$ viscosity, $\gamma$ the CO$_2$-water interfacial tension, and $\theta$ the water contact angle on mineral surface.

Viscosity ratio shows the mobility ratio of the injected CO$_2$ and defending brine, and is defined as:

$$M = \frac{\mu_{CO_2}}{\mu_{Brine}}$$ \hspace{1cm} (2-6)

where $\mu_{CO_2}$ and $\mu_{Brine}$ are viscosity of CO$_2$ and brine respectively. $M$ is the viscosity ratio of CO$_2$ to brine.
Lenormand et al. (1988) proposed a diagram called “phase-diagram” to visualize the displacement regime based on the abovementioned capillary number and viscosity ratio, which categorizes the three displacement regimes (Fig. 2.3): (1) viscous fingering: when capillary number is large (capillary forces are much higher than viscous forces) and viscosity ratio is small (the injecting fluid has much lower viscosity than existing fluid), the injected fluid has a dendritic pattern in the interface with the defending fluid and the unstable front of the injected fluid propagates along with the flow, (2) capillary fingering: when capillary number is small and no matter of viscosity ratio value, the high capillary forces control the flow pattern, which seems to unstable like viscous fingering condition. But here capillary fingers develop in every direction not just along main flow, (3) stable displacement: when both capillary number and viscosity are large, the interface of the injected fluid and defending fluid is stable and perpendicular to the flow path [Lenormand et al., 1988; Ferer et al., 2004; Cottin et al., 2010; Heiß et al., 2011; Zhang et al., 2011a; Kazemifar et al., 2016].

When the displacement pattern is one of the two fingering regimes, the large portion of the resident brine is not swept that results in low sweep efficiency. Many efforts have been focused on a better understanding of the fluid displacement mechanisms and increase of the injection efficiency by achieving stable displacement flow pattern [Lenormand et al., 1988; Polak et al., 2011; Wang et al., 2011; Cao et al., 2016]. Details are followings;

CO₂ injection rate: Higher CO₂-brine displacement during CO₂ injection and higher residual CO₂ saturation after the completion of CO₂ injection are observed by increased injection rate during drainage condition [Polak et al., 2011; Soroush et al., 2014; Cao et al., 2016]. However, the danger of wellbore damage should be considered during pressure increase for higher injection rate.
CO$_2$ viscosity: one of the most challenging issues in sweep efficiency of GCS in saline aquifers is lower viscosity of CO$_2$ than that of brine, which causes viscous and capillary fingerings during CO$_2$ injection [Kazemifar et al., 2016]. Thus, in order to increase the viscosity of CO$_2$, thickener materials have been considered such as toluene, fluoroacrylate-styrene copolymer (polyFAST), and polymers [Zhang et al., 2011c; Enick, Robert M., Olsen, 2012], which have shown a great impact on the increase of CO$_2$ viscosity. For example, just one percent concentration of fluoroacrylate leads to 10 times increase in CO$_2$ viscosity [Enick, Robert M., Olsen, 2012].
**CO₂ Foam.** The injected CO₂ prefers to percolate through large pores in porous media, which reduces sweep efficiency in saline aquifers [Benson et al., 2005]. CO₂ foam is a solution to solve the problem of escaping CO₂ through large pores and fissures during injection. CO₂ foam consists of CO₂ droplets and aqueous lamella surrounding the dispersed droplets. The foam can block large spaces and enforce the injected CO₂ to sweep smaller pores. As a result, sweep efficiency increases [Enick, Robert M., Olsen, 2012]. Also, CO₂ foam has a higher viscosity than supercritical CO₂, which cause capillary number and viscosity ratio to increase [Enick, Robert M., Olsen, 2012]. CO₂ foam has been studied for enhanced oil recovery (EOR) by mixing with injected water and a surfactant or a polymer [Elhag et al., 2014; Bal et al., 2015]. For example, a new polymer, a surface-modified nanoparticles, and surfactants have been developed for a better stabilization of CO₂ foam under high salinity and temperature [Song et al., 2014; Worthen et al., 2014; Xu et al., 2016]. The studies related to CO₂ form injection with a surfactant or a polymer in GCS should be required.

**Surfactant.** Surfactants have been developed to decrease the interfacial tension between injected CO₂ and brine in saline aquifers, which change capillary number and viscosity ratio to reach stable pattern of displacement. Also, surfactant increases the CO₂ foam viscosity with several order of magnitudes when mixed with CO₂ foam [Ren et al., 2013]. It can be injected directly with supercritical CO₂ into saline aquifers for conformance control [Enick, Robert M., Olsen, 2012].

**Nano particles.** An inexpensive nanoparticles have been considered as an economic solution to increase stability of the CO₂ foam, which can be prepared with silica coated by polyethylene glycol (PEG) [Enick, Robert M., Olsen, 2012]. Surfactants mostly used for stabilizing CO₂ foam, but they have a limitation due to their absorption on rock surface and degradation in high temperature and salinity. However, nano-particles including nano-silica particles tend to adsorb at
the liquid-gas interface (at the lamella made of water) and form a protective barrier around CO₂ droplet. This barrier prevents the dispersed droplet of CO₂ to be coalesced [Dickson et al., 2004; Lee et al., 2015].

2.4 Visualizing Experiments for Two-phase Immiscible Flow

Knowledge of an immiscible two-phase fluid flow displacement in a porous medium is of importance for many natural and engineering systems like water infiltration in soils and rocks [Whitaker, 1986], groundwater contamination [Mercer and Cohen, 1990], enhanced oil/gas recovery (EOR) [Luckner et al., 1989], methane hydrate extraction [Burshears et al., 1986], and geological CO₂ sequestration [Krevor et al., 2015a; Cao et al., 2016].

Experimental studies have been conducted to manipulate the parameters contributing to capillary number and viscosity ratio and to explore its effects on the displacement patterns. Details are following;

2.4.1 2D Micromodel:

The two dimensional micromodel consists of several cylindrical or cubic materials that are trapped between two transparent plates at top and bottom. The packed material represents grains of soil or rock and the gap between them acts as pores between grains with rectangular or circular pore throats. The top and bottom plates are sealed and have an inlet and an outlet so that fluid can be injected and flow among the pores as channels. Either homogeneous or heterogeneous patterns of channels are available [Zhang et al., 2011a]. In new micromodels, customized pore networks are etched on two symmetrically patterned plates that are fused together to form a two-dimensional porous network [Cao et al., 2016]. This set up called 2D micromodel can be made of using (1)
glass that is representative of silica sand or sandstone; (2) coated glass containing hydrophobicity on the surface [Ferer et al., 2004; Chalbaud et al., 2009; Riazi et al., 2011]; or (3) other materials such as silicon, polyester resin, and acrylic materials coated with silicate [Lenormand et al., 1983, 1988; Willingham et al., 2008; Chang et al., 2009; Cottin et al., 2010; Zhang et al., 2010]. While buoyancy effect is negligible, other parameters such as viscosity of injected CO₂, flow rate, and injection pressure are controlled (Eqn. 2-5 and 2-6). Images of flow pattern and sweep efficiency are monitored using a high-resolution camera or a microscope. In order to obtain better distinguishable images using a fluorescent microscopy, fluorescent dye is used in fluids [Wang et al., 2013c; Zuo et al., 2013; Kazemifar et al., 2016].

While micromodels have the mentioned benefits, they only can model two-dimensional fluid flow. They also have uniform depth of channels and physically and chemically homogenous surface in channels. The pore sizes are also mostly limited to values higher than 10 μm [Kim et al., 2012].

2.4.2 3D X-ray Tomography and Magnetic Resonant Imaging

X-ray computed tomography (CT) or magnetic resonance imaging (MRI) has been used to derive a 3D image of the pores and fluids flow in pore throats from a rock core or other porous materials like coal [Jikich et al., 2003; Perrin and Benson, 2010; Golab et al., 2012; Song et al., 2013; Wildenschild and Sheppard, 2013; Herring et al., 2013, 2014; Nakagawa et al., 2013; Bray et al., 2014; Vogt et al., 2014; Roels et al., 2014; Manceau et al., 2015; Ott et al., 2015]. While this method has a limitation of lower resolution of images rather than 2D transparent micromodels [Kazemifar et al., 2016], it has the significant advantage of considering heterogeneity of in-situ samples, such as pore surface material heterogeneity and heterogeneity in permeability originated from variation in pore sizes, spatial distribution, texture, and connectivity [Zhang et al., 2011b].
2.5 Monitoring and Safety Control

Leakage of CO₂ from a storage site is the main safety concern of GCS because of environmental hazards as well as nullification of the whole project purpose. A leakage of CO₂ from deep ground layers can pollute and acidify shallower underground freshwater resources. Moreover, lowering the pH of freshwater can result in release of harmful metals in water [Little and Jackson, 2010]. Surface leakage also has environmental problems. Density of CO₂ is higher than that of air, so after leakage, it can accumulate in pits and depressions (CO₂ density is 1.842 kg/m³ and air density is 1.205 kg/m³ at sea level and at 20° C). Adverse physiological effects can happen
for human at CO$_2$ concentration of 3% and increasing it to 10% have fatal effects. For instance, due to volcanic activity, a sudden release of 100 kilotonnes of CO$_2$ in Lake Nyos, in Cameroon, killed 1700 people [Wilson et al., 2003]. While 0.01 to 0.1% leakage values per year seem to meet CO$_2$ storage objectives, the acceptable leakage value for environmental aspects and health safety depends on local conditions [Chow, 2003; Etheridge et al., 2005; White et al., 2005]. Thus, a long-term monitoring plan in all storage sites is required at the beginning of projects. The monitoring can be conducted at subsurface, on the surface, or above the surface. In the subsurface, well-pressure monitoring, geophysical seismic tests, and numerical simulation of CO$_2$ migration can be used [Dodds et al., 2009; Zhang et al., 2013; Brown, 2014; Kaven et al., 2014]. On the surface, the concentration of the CO$_2$ can be measured by gathering the sample of the air [Seto and McRae, 2011; United States Department of Energy National Energy and Laboratory Technology, 2012]. Above the surface, the remote sensing method can be applied to measure CO$_2$ leakage directly or indirectly [Zahid et al., 2011; Verkerke et al., 2014]. While direct method is to measure CO$_2$ leakage, indirect methods is to monitor the change of anomalies, surface deformation, and vegetative stress [Verkerke et al., 2014]. Thermal anomalies can occur when heated CO$_2$ migrated from underground or a localized freezing happens due to rushing gases leakage [Verkerke et al., 2014]. Because of injection, a uniform swelling of surface corresponding to the injection rate in the region is expected. An inconsistent deformation or swelling rate could be a sign of leakage. Using interferometry, several maps of the storage site surface are prepared and compared each other to monitor surface deformation [Verkerke et al., 2014]. Vegetation stress is the quantifying environmental effects on a plant health. It includes any factors that could cause to death of plants like lack or too much coldness, heat, water, sunlight, fertilizer and so on. A plant under stress means it is subjected to non-ideal growing conditions. Mapping of vegetation stress may reveal
leakage location precisely as the high amount of CO\textsubscript{2} has negative effects on the plants growth [Verkerke et al., 2014].

Key criteria for safety, environment, and health related concerns of a geological storage site have been developed based on the laws [Seligsohn et al., 2010]. Details are as follows; (1) monitoring program should be designed and regulated for each site specifically because of site dependency of GCS projects. Also, monitoring plan should be continuously updated through reassessing of the site conditions to keep storage site safety due to dynamic behavior of the injected CO\textsubscript{2} and reservoir; (2) data of reservoir conditions should be collected during CO\textsubscript{2} injection and future expected behavior must be predict; (3) possible pathways of CO\textsubscript{2} leakage including natural faults and drilled boreholes should be considered and a versatile risk assessment should be conducted; (4) the boundary of monitored area should not be limited to the injected CO\textsubscript{2} plume. All the regions that undergo any change such as pressure increase in pore fluids must be continuously observed; (5) the frame work of site monitoring after completion of CO\textsubscript{2} injection must determine responsibilities, the time of effectiveness of regulations, reaction to an accident or any leakage, and liability for reimbursement and fines; and (6) local and nationwide public engagement is crucial [Seligsohn et al., 2010].

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Chapter 3. The Change in Contact Angle at Unsaturated CO2-water Conditions: Implication on Geological Carbon Dioxide Sequestration

3.1 Introduction

Carbon dioxide as a greenhouse gas is the main source for global warming. CO₂ emission has been considered as a serious concern due to the increase in atmospheric temperature. Despite of huge efforts of governments to develop clean energies, the dependence on fossil fuels increases because of the excessive energy demand. Carbon capture and storage (CCS) technique is one of alternatives to decrease CO₂ emission [Bachu et al., 1994; Pacala and Socolow, 2004]. CCS method includes the process of separating and capturing CO₂ in the industry, and transferring it to store in different forms [Bachu et al., 1994]. Among various methods of CCS, geological CO₂ sequestration (GCS) is considered as a promising method to control CO₂ emission for a long time in large scale [Bachu et al., 1994, 2007; Bachu, 2000a; Holloway, 2005, 2007; Godec et al., 2011]. The main idea of GCS is to trap CO₂ into deep sites for hundreds to thousands of years in a safe [IPCC, 2005; Michael et al., 2010]condition. Depleted oil and gas reservoirs, saline aquifers, deep coal seams, and deep ocean sediments are main candidates as CO₂ storage sites [Bachu, 2000b; Pashin and McIntyre, 2003; Massarotto et al., 2010; Tang et al., 2014]. Among them, saline aquifers have been focused due to its enormous storage capacity [Michael et al., 2010]. CO₂ can be trapped by several mechanisms such as structural trapping, residual capillary trapping, solubility trapping, and mineral trapping [Saraji et al., 2013b].

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In short term, storage capacity is controlled by structural and capillary trappings [Bandara et al., 2011], which are governed by capillary pressure, because capillary pressure between CO$_2$ and water (or other fluids) phases entraps both connected CO$_2$ plume below the caprock and disconnected CO$_2$ bubbles in formation pores [Krevor et al., 2015b]. Also, capillary pressure contributes to the safer long-term trapping mechanisms by solubility and mineral trapping [Akbarabadi and Piri, 2015]. Capillary pressure between CO$_2$ and water in GCS can be explained by the Young-Laplace equation as below:

\[
P_C = P_{CO_2} - P_{water} = \frac{2\gamma_{water-CO_2}\cos(\theta)}{R}
\]

Where $P_C$ is capillary pressure, $P_{CO_2}$ is CO$_2$ pressure, $P_{water}$ is water pressure, $\gamma_{water-CO_2}$ is the water-CO$_2$ interfacial tension, $\theta$ is the water contact angle on mineral surface, and $R$ is pore radius.

The pore radius $R$ varies at different storage sites and can be estimated. The interfacial tension between CO$_2$ and water has been reported as 20–35mN/m in the pressure and temperature ranges of GCS sites [note: pressure range of 6–20 MPa and temperatures below 71°C [Bachu and Bennion, 2009; Bachu and Brant Bennion, 2009; Chalbaud et al., 2009; Jafari et al., 2016]. While the contact angle has been studied at a variety of GCS conditions, reported values have shown a significant discrepancy. Recent reports indicate that mineral wettability changes with the presences of CO$_2$; however the results are still highly discrepant to each other. For example, while a few studies present no distinctive correlation between CO$_2$ pressure and contact angle change on silica substrates [Espinoza and Santamarina, 2010; Broseta et al., 2012; Farokhpoor et al., 2013a, 2013b; Wang et al., 2013b; Kim and Santamarina, 2014], others report that the contact angle on silica substrates increases with the increased CO$_2$ pressure [Chiquet et al., 2005; Dickson et al., 2006; Siemons et al., 2006; Shah et al., 2008; Yang et al., 2008a; Jung and Wan, 2012; Iglauer et al., 2014; Al-Yaseri et al., 2015; Sarmadivaleh et al., 2015]. Especially, Jung and Wan (2012)
showed that the average net increase in contact angle is $17.6^\circ \pm 2.1^\circ$ with the increase of pressure from 0.1 MPa to 25 MPa. Also, the average net increase of $19.6^\circ \pm 2.1$ in contact angle is observed with the increase in ionic strength from 0 M to 5 M [Jung and Wan, 2012]. However, Chiquet et al. [2007] presented that salinity did not affect the quartz wettability considerably.

This inconsistency of contact angles among previous studies is more distinct when mica is used in experiments. Though reported data show that pressure affects both advancing- and receding-contact angles on mica substrates [Broseta et al., 2012], the effects of pressure and salinity on the contact angle are not clear yet. Wan et al. (2014) presented the sources of uncertainty in contact angle on mica substrates relevant to GCS conditions, which include the effects of initial soundness of mineral surface, uncleanness and defeat during experimental process, dissolution of CO$_2$ bubble, fluids saturation, repetition and CO$_2$ time exposure contacting with mineral, wettability change on mineral surface, and substrate roughness change due to the reaction with CO$_2$.

Ideally, contact angle, which is related to the interfacial properties of the solid, liquid and gas based on Young’s equation, is independent to the droplet size and mass on the homogeneous, isotropic, and smooth mineral surface [Nadkarni and Garoff, 1992; Kwok and Neumann, 1999]. However, many reports have shown that contact angle depends on the droplet size, surface roughness, and chemical heterogeneity on mineral surface due to non-ideal conditions on mineral surfaces [Gaydos and Neumann, 1987; Lin et al., 1993; Li, 1996b]. Advancing- and receding-contact angles increase with the decreased water droplet size [Herzberg and Marian, 1970; Good and Koo, 1979], and a nonlinear relation between $\cos \theta$ and $1/r$ was suggested, where $\theta$ is contact angle and $r$ is droplet radius [Drellich et al., 1993]. The dependence of contact angle on the droplet size has been explored based on (1) line tension theory [Gaydos and Neumann, 1987; Li and
Neumann, 1990; Li, 1996a], (2) buoyancy or gravitational effect [Vafaei and Podowski, 2005a, 2005b], and (3) triple line (or contact line) [Tadmor, 2004; Wan et al., 2014].

Line tension is introduced with an analogue of surface tension for two dimensional surface as the free Gibbs energy per unit length of the three-phase contact line or as the force operating in three-phase contact line in one dimension [Li and Neumann, 1990; Weijs et al., 2011]. Good and Koo (1979) presented the line tension theory with a relationship between contact angle and droplet size, which was modified from Young’s equation and is shown in the equation 3-2 (Fig. 3.1) [Good and Koo, 1979; Gaydos and Neumann, 1987; Li and Neumann, 1990; Drelich et al., 1993; Lin et al., 1993]:

$$\gamma_{lg} \cos \theta = \gamma_{sg} - \gamma_{ls} - \frac{\sigma}{R}$$ (3-2)

Where $\gamma_{lg}$, $\gamma_{sg}$, and $\gamma_{ls}$ are interfacial tension between liquid and gas, solid and gas, and liquid and gas, respectively. $\sigma$ is line tension ($J$) and $R$ is triple phase line radius (Fig. 3.1).
When the droplet size is large enough, \( R \) can be assumed as infinity and the equation 3-2 can be changed to:

\[
\gamma_{lg} \cos \theta_\infty = \gamma_{sg} - \gamma_{ls}
\]  

(3-3)

Where \( \theta_\infty \) is the contact angle of a droplet with infinity radius of contact line. A relation between contact angle and droplet radius is explained by combining the equations 3-2 and 3-3 as below [Kaveh et al., 2014]:

\[
\cos \theta = \cos \theta_\infty - \frac{\sigma}{R \gamma_{lg}}
\]  

(3-4)

The contact angle of a droplet with infinity radius and line tension can be obtained using the plot of \( \cos \theta \) versus \( 1/R \), which offers a simple relation between contact angle and droplet size; however, different experimental studies have shown a wide range of line tension magnitude and the sign due to the high uncertainty in data and the difficulty in measurement. For example, a small non-homogeneity results in the wide value range of line tension values (i.e. \( 10^{-11} \) to \( 10^{-5} \) J/m) [Kaveh et al., 2014]. The imperfection of a solid surface including chemical heterogeneity, roughness, and anisotropy causes the extensive discrepancy in line tension values [Herzberg and Marian, 1970; Drelich et al., 1993; Lin et al., 1993; Lin and Li, 1995; Nakae et al., 1998]. Thus, the line tension theory has been considered as an oversimplification theory to correlate the contact angle and the droplet size [Tadmor, 2004].

Buoyancy (gravity) effect has been considered to correlate contact angle and droplet size and to overcome the problem of imperfect surfaces [Vafaei and Podowski, 2005a, 2005b]. Vafaei and Podowski (2005b) proposed the relation between the droplet size and contact angle based on a theoretical work on the axisymmetric droplets as blow, which was verified by a series of experiments:
\[
\sin \theta = \left[ \frac{3V}{\pi(2+\cos \theta_S)(1-\cos \theta_S)^2} \right]^{\frac{1}{3}} \frac{\sin^2 \theta_S}{R}
\] (3-5)

Where, \( V \) and \( R \) are the volume and the radius of a droplet respectively, and \( \theta_S \) is the contact angle of a spherical droplet when the volume is small enough to disregard the gravity effect.

Both gravity force and surface force influence droplet shape and contact angle. Thus, a dimensionless Bond number, was defined considering the gravity force and the surface [Kaveh et al., 2014]:

\[
B_O = \frac{\Delta \rho g l^2}{\gamma_{lg}}
\] (3-6)

where, \( Bo \) is a dimensionless number, \( \Delta \rho \) is the difference between liquid and gas densities, \( L \) is a characteristic length which equals to the diameter of a liquid droplet (or a gas bubble), and \( \gamma_{lg} \) is the liquid-gas interfacial tension.

Shojai Kaveh et al., [2014] presented that droplet size and Bond number decrease during CO\(_2\) dissolution in unsaturated condition, which causes water contact angle to increase until Bond number decreases up to 0.9. And then, contact angle remained relatively constant when the Bond number was smaller than 0.9. The results separated two regimes: contact angle change during CO\(_2\) dissolution, and relatively constant contact angle during gradual diffusion [Kaveh et al., 2014]. However, the relation between droplet size and contact angle was not observed when the rough surface material was used [Kaveh et al., 2014]. Furthermore, other studies showed a discrepancy. For example, the gravity did not affect the contact angle of a droplet [Herzberg and Marian, 1970; Blokhuis et al., 1995; Fujii and Nakae, 1995].

The role of imperfection of mineral surfaces on contact angle has been studied considering triple line (or contact line) that was defined as the line where the three phases of solid substrate, liquid, and gas contact (Fig. 3.1) [Tadmor, 2004; Wan et al., 2014]. Tadmor [2004] stated that the
pinning effect of triple line is a resistance against the triple line motion due to blemishes. The
ergies that governs the triple line (or contact line) can be categorized as an elastic energy due to
liquid/vapor surface tension and a pinning energy as a result of the preference of the solid substrate
for either the phases of liquid or vapor, which affect contact angle [Nadkarni and Garoff, 1992].

In geological CO₂ sequestration, injected CO₂ dissolves into brine, which decreases the CO₂
droplet volume to decrease at the pinned triple line, and increases water contact angle. When the
interfacial tension between CO₂ and water overcomes the resistance of pinned triple line, the triple
line moves to CO₂/solid interface on the mineral surface. And then, when triple line reaches the
point that a substrate prefer to attract liquid more than gas, the triple line does not move anymore
(i.e. pinned at the point). The sticking, stretching, and jumping of triple line result in the change
of the CO₂ droplet shape and water contact angle [Wan et al., 2014]. For example, contact angle
on the mica substrate increases rapidly with CO₂ dissolution at the constant triple line length
(pinned status), and then remains constant when the length of the contact line decreased (slipped
status) [Lam et al., 2002b; McHale et al., 2005; Kulinich and Farzaneh, 2009]. Saghafi et al.,
(2014b) also observed two clear stages of the triple line motion and contact angle change on the
coal substrate during CO₂ dissolution into water. Also such contact angle change and the stick-slip
behavior of triple line have been observed on the silicon wafers substrate which is attributed to the
chemical bond between fluid and solid surfaces at the contact line [Lam et al., 2002a].

While previous studies have measured contact angles using the fully CO₂-saturated brine
system [Chiquet et al., 2005; Siemons et al., 2006; Dickson et al., 2006; Shah et al., 2008; Yang et
al., 2008b; Espinoza and Santamarina, 2010; Broseta et al., 2012; Jung and Wan, 2012; Saraji et
al., 2013b; Wang et al., 2013b; Farokhpoor et al., 2013a, 2013b; Iglauer et al., 2014; Kim and
Santamarina, 2014; Al-Yaseri et al., 2015; Sarmadivaleh et al., 2015], CO₂ and brine should be
unsaturated to each other when CO₂ is injected into saline aquifers, associated with CO₂ dissolution and droplet size decrease. Also, contact angle should be changed during CO₂ dissolution. In this study, we consider the triple line together with shape and size of CO₂ droplet to explore their effects on the contact angle, to identify the inconsistency among reported contact angles, and to anticipate the reasonable contact angles in the unsaturated geological CO₂ storage. Thus, three dimensions of a CO₂ droplet such as contact line diameter (CLD), droplet height (H), and droplet diameter (D) are introduced to consider CO₂ droplet shape and size, and pinning effects together.

3.2 Experimental Studies

The laboratory experiments are being performed in the geotechnical research lab at LSU to investigate silica and mica contact angle measurement to aim to wettability behavior of rocks under CO₂ sequestration condition. To conduct the experiment the following tasks are necessary: (1) material preparation, (2) apparatus and set-up preparation, (3) selection and execution of specific testing procedures.

3.2.1 Material Preparation

For contact angle measurement, silica and mica substrates were used, which are the most common minerals found in rock formations. The silica substrates, which are a smooth fused amorphous SiO₂, are prepared from VWR VistaVision, and the two muscovite mica types of V1 and V5 [Note that V1 and V5 represent the highest and the lowest purity on mica surfaces, respectively] are prepared from Electron Microscopy Science. The visual quality description of mica V1 and V5 grade are as follow [ASTM, 2015]:

V1: “Clear—Hard, of uniform color, flat, free from all stains and foreign inclusions, waves, cracks, buckles, and other similar defects.” [ASTM, 2015]
V5: “Stained A Quality—Hard, free of cracks and other similar defects and foreign inclusions, except may be medium wavy and may contain slight vegetable stains and the entire area may have air inclusions if not heavily concentrated. Crystallographic discoloration is permitted.” [ASTM, 2015]

These ruby and brown colored muscovite mica has priority to use compared with green muscovite because of hardness and better cleavage properties allowing it to be split into very thin films without generating any cracks. It also remains elastic and tough even in high temperature after splitting into thin films along with cleavage plane.

The silica and mica sheets have the dimension of 25 mm by 25 mm and the thickness of 0.23mm ~ 0.3mm (Fig. 3.2). The Table 3.1 and Table 3.2 present the typical physical and mechanical properties of the Mica V1, respectively.

Figure 3.2. Substrates used in the experiments: (a) silica (b) mica V1 and V5
Table 3.1. Typical physical properties of the Mica V1 [Electron Microscopy Sciences]

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness: Moh's scale:</td>
<td>2.8 - 3.2</td>
</tr>
<tr>
<td>Shore's Test:</td>
<td>80 - 150</td>
</tr>
<tr>
<td>Specific Gravity, g/cm³:</td>
<td>2.6 - 3.2</td>
</tr>
<tr>
<td>Tensile Strength, kg/cm²:</td>
<td>~ 1750</td>
</tr>
<tr>
<td>Compression Strength, kg/cm²:</td>
<td>1900 - 2850</td>
</tr>
<tr>
<td>Refractive Index (air=1):</td>
<td>1.56 - 1.60/61</td>
</tr>
<tr>
<td>Dielectric Strength @ 20°C in volt/mil:</td>
<td>3,000 - 6,000</td>
</tr>
<tr>
<td>Maximum Thermal Resistance:</td>
<td>625°C</td>
</tr>
<tr>
<td>Modulus of Elasticity, kgf/cm²(× 10⁻³):</td>
<td>1400 - 2100</td>
</tr>
<tr>
<td>Optic Axial Angle:</td>
<td>50° - 75°</td>
</tr>
<tr>
<td>Coefficient of Expansion per °C:</td>
<td>Perpendicular to cleavage plane 9E(-4) - 36E(-4)</td>
</tr>
<tr>
<td>Calcining Temperature</td>
<td>700 - 800°C</td>
</tr>
<tr>
<td>Thermal Conductivity:</td>
<td>~0.0013</td>
</tr>
<tr>
<td>Water of Constitution, %:</td>
<td>4 - 5</td>
</tr>
<tr>
<td>Moisture Absorption:</td>
<td>Very low</td>
</tr>
<tr>
<td>Apparent Electric Strength:</td>
<td>120 - 200kV/mm</td>
</tr>
<tr>
<td>Permittivity @ 15°C :</td>
<td>6 - 7</td>
</tr>
<tr>
<td>Power Factor (loss Tangent) @15°C:</td>
<td>0.0001 - 0.0004</td>
</tr>
<tr>
<td>Volume Resistively @25°C Ohm.cm:</td>
<td>4 × 10⁻¹⁵ - 2 × 10⁻¹⁷</td>
</tr>
<tr>
<td>Acid Reaction:</td>
<td>Affected by HF</td>
</tr>
</tbody>
</table>

Table 3.2. Chemical composition of a typical mica V1 [Electron Microscopy Sciences]

<table>
<thead>
<tr>
<th>Chemical component</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (SiO₂)</td>
<td>45.57</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>33.10</td>
</tr>
<tr>
<td>Potassium Oxide (K₂O)</td>
<td>9.87</td>
</tr>
<tr>
<td>Ferric Oxide (Fe₂O₃)</td>
<td>2.48</td>
</tr>
<tr>
<td>Sodium Oxide (Na₂O)</td>
<td>0.62</td>
</tr>
<tr>
<td>Titanium Oxide (TiO₂)</td>
<td>Traces</td>
</tr>
<tr>
<td>Calcium Oxide (CaO)</td>
<td>0.21</td>
</tr>
<tr>
<td>Magnesia (MgO)</td>
<td>0.38</td>
</tr>
<tr>
<td>Moisture at 100°C</td>
<td>0.25</td>
</tr>
<tr>
<td>Phosphorus (P)</td>
<td>0.03</td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td>0.01</td>
</tr>
<tr>
<td>Graphite Carbon (C)</td>
<td>0.44</td>
</tr>
<tr>
<td>Loss on Ignition (H₂O)</td>
<td>2.74</td>
</tr>
</tbody>
</table>
Figure 3.3 presents a SEM image of the mica plate, which shows high heterogeneity and roughness of the mica surface, especially in case of the mica grade V5. More blemishes are observed on the surface of the mica V5.

![Figure 3.3. SEM image of the mica sheets: (a) V1; (b) V5](image)

Figure 3.4 shows an AFM image used for determining the roughness of an area of 50µm×50µm for the two mica plates. The surface roughness of mica was measured twice, and the average roughness is 0.192 ± 0.013 and 0.218 ± 0.018 nm for the mica V1 and V5, respectively. For fluids, deionized water and brine with NaCl (Aldrich) with molarities of 0, 1, and 3 M and CO₂ with 99.99% purity were prepared.
3.2.2 Contact Angle Measurement Test Methods

There are several different methods to measure contact angle on a flat plate including: [Tretinnikov and Ikada, 1994; Erbil et al., 1999; Rao and Karyampudi, 2002; Yuan and Lee, 2013]

1) Sessile drop
2) Captive bubble method
3) Tilting pate method
4) Wilhelmy balance method
5) Several new modified method like dual-drop dual-crystal contact angle technique

The high pressure condition needed for the geological CO\textsubscript{2} sequestration limits using some methods like Wilhelmy method; thus, sessile drop and captive method are mostly used in geological CO\textsubscript{2} sequestrations studies. In the present research, a captive bubble test method is selected because of higher reproducibility (Lv et al. 2017), and also for the reason of resemblance to a real condition of CO\textsubscript{2} injection into an aquifer, in which the aquifer has been already saturated by water/brine and then CO\textsubscript{2} is introduced by injection.

Figure 3.4. AFM image (measured area is 50µm×50µm) a) Mica V1 b) Mica V5
3.2.3 Experimental Set-up

A high pressure chamber is needed for a captive test which needs to meet the strength, sustainability, and workability required for simulating the thermodynamic of a geological CO$_2$ sequestration. Stainless steel was selected for the chamber material because of high tensile strength and the less risk of corrosion due to contact with saline and acidic water. Requirements to seal the chamber against leakage for both gas and liquid has been considered in O-rings design. The designed chamber was built in the LSU mechanical engineering machine shop. The high-pressure chamber had two glass windows allowing taking the images of a CO$_2$ or water droplet on a substrate during tests. The substrate was placed onto a welded plate located inside the chamber. By rotating the chamber, the position of the substrate inside the chamber can be placed on the bottom part and needle in the top of chamber. This configuration is used for a sessile drop test in which the chamber is filled with gas first and then a drop of water through the needle is fallen from top on the substrate. If the substrate is placed in the top and needle in the bottom by rotation, the configuration is used for a captive sessile test in which the chamber is filled by water or brine first and then a bubble of CO$_2$ is injected through the needle from bottom and the bubble moves upward due to buoyancy and sticks under the substrate. The figure 3.5, figure 3.6, and figure 3.7 shows the high pressure chamber, entire set-up, and the schematic experimental set-up.
Figure 3.5. The high-pressure chamber used for contact angle measurement

Figure 3.6. The set-up for contact angle measurement.
The chamber is totally cleaned with deionized water before each test. The substrates are cleaned with an isopropyl alcohol before each test, and are carried with gloves and tweezers to avoid unexpected contaminations. To ensure the reproducibility of the experiments, the substrates are used only once for every test. To make sure no contamination and additional chemical are existed in the system, no glue is used to fix the substrate on holding plate in the chamber. We use a clipper to keep the substrate.

The chamber pressure was provided from a top-port connected to a precise high-pressure syringe pump (Teledyne ISCO, 500 HP) and a CO₂ bubble was placed under the substrate from top or bottom-port of the chamber through a needle. The chamber pressure was measured by an
OMEGA PX309-3kGV pressure transducer (up to 3000psi ≈ 20MPa capacity and accuracy of 0.25% of the capacity). The time-lapse change in bubble shape was recorded using a high-resolution camera (16.2 Mega Pixel, Nikon D5100 and Nikon D7000) through transparent glass windows. The set-up was placed on a stable table and the chamber was placed on a wooden base and constrained with the rubber to minimize any vibration effects. Whole the set-up were placed inside of a thermal insulating box for preventing temperature exchange. The temperature remained constant using a heating gun and two heating lights, which were connected to a traceable temperature controller. The temperature variations were measured using four K-type (Nickel-Chromium / Nickel-Alumel) thermocouples inside the thermal insulating box, which made sure that all temperatures of an experimental set-up were constant during tests. The variations of temperature and pressure were recorded every one second using a data logger.

### 3.2.4 Experimental Procedure

After fixing the substrate to the plate, the chamber is assembled carefully. The chamber is flushed with CO₂ to assure there is no air in the system. Then the chamber is filled with deionized water which is not pre-saturated with CO₂ to simulate the short-term wettability behavior in CO₂ storage site, and then the system is pressurized 1~10 MPa using the ISCO-pump. CO₂ is in gaseous state within the range of 1 MPa ~ 5MPa. CO₂ is in supercritical condition at 10 MPa pressure, and a transient condition between gaseous and supercritical condition at 7 MPa pressure. The set-up was balanced with the target temperature for 4 hours. CO₂ was injected through the needle attached on the bottom of chamber and a CO₂ droplet formed under the silica substrates gently. The camera captured the CO₂ droplet every 2 seconds during tests. Contact angle was measured using ImageJ (an image processing software) with a plugin function (a contact angle measurement function) to
fit the best circle or ellipse on the CO$_2$ droplet [Note. the accuracy and repeatability of ImageJ were verified by [Lamour et al., 2010; Williams et al., 2010]. The average of contact angles in two side of the CO$_2$ droplet was reported. Both dimension and volume of the droplets were determined using AutoCAD. The contact angle estimation from images was stopped when the droplet volume was less than 0.15 mm$^3$ due to the low image resolution. After each test, the chamber was disassembled and was completely cleaned. For the mica substrate, the above procedures were followed except for the case of high temperature (45ºC) and salinity (1M NaCl).

3.3 Results and Discussions

Figure 3.8 presents that the CO$_2$ droplet dissolves into water, which causes the volume of CO$_2$ droplet on both silica and mica substrates to decrease. At the same time, the contact angle on silica substrate initially increases with the decreased volume of the CO$_2$ droplet, and then remains relatively constant. The variation of contact angle on silica substrate has small range from 34.5º to 42.1º (Fig. 3.8a,b,c). However, the contact angle on mica substrate continuously increases with the decreased volume of CO$_2$ droplet. Also, the variations of contact angle on mica substrate range from 25.4º to 68.1º (Fig. 3.8d,e,f).

Constantly remaining contact angle on silica substrate after initially increasing according to the decreased volume of CO$_2$ droplet can be explored through the effect of gravity on the droplet shape [Vafaei and Podowski, 2005a, 2005b]. Initially large size of a CO$_2$ droplet can be squeezed by buoyancy force (or gravity force) that originated from the density difference between CO$_2$ and water in a captive sessile test, which causes smaller initial water contact angle. CO$_2$ droplet size decreases according to the dissolution of CO$_2$ droplet into water, which cause contact angle to increase and then to remain constant with the small volume change of CO$_2$ droplet when the
buoyance effect can be disregarded (Fig. 3.8a,b,c). However, contact angle on mica substrate continuously increases with the decreased volume of a droplet. Thus, this chapter explores the factors to influence on the variation of contact angle instead of the volume change of CO$_2$ droplet.

Figure 3.8. The variations of CO$_2$ droplet volume and contact angle according to time change, (a) silica at 1 MPa pressure and pure water during the first test, (b) silica at 1 MPa pressure and pure water during the second test, (c) silica at 1 MPa pressure and pure water during the third test, (d) mica at 5 MPa pressure and 1 molarity saline water, (e) mica at 7 MPa pressure and 1 molarity saline water, (f) mica at 10 MPa pressure and 1 molarity saline water.
3.3.1 Relations between Contact Angle and Droplet Shape

Figure 3.1 shows a CO₂ droplet surrounded by water, which consists of three dimensions such as contact line diameter (CLD), droplet diameter (D), and droplet height (H). The CLD is the diameter of the triple line in the profile of a droplet [Note. triple or three-phase line is the line of contact among three phases of solid (substrate), liquid (water) and, vapor (CO₂), which can be in gaseous, liquid, and supercritical condition depending to the pressure and temperature] [Good, 1979].

The droplet diameter (D) and height (H) are the maximum diameter of a droplet in horizontal- and vertical-directions, respectively. Figure 3.9 presents the variations of contact angle and the three dimensions at different time. Figure 3.9a,b,c show the results of three sequential CO₂ droplet tests on the same silica substrate at 1MPa pressure. The second CO₂ droplet formed after the completion of the first test without disassembling the chamber, and the third test was repeated after the second CO₂ droplet disappeared. Figure 3.9d,e,f show the results of CO₂ droplets on mica substrates at a variety of pressure (i.e. 5MPa to 10MPa). New mica substrate was replaced whenever the test was completed.

The results show that (1) all three dimensions generally decrease with time due to CO₂ dissolution into water; (2) while the first and the second CO₂ droplets on silica substrate show fast dissolution, the third CO₂ droplet shows slow dissolution during 150 sec after CO₂ droplet forms (Fig. 3.9a,b,c); (3) droplet diameter (D) and height (H) decrease continuously on both silica and mica substrates; (4) the contact line diameter (CLD) remains initially constant values and then decreases unlike both droplet diameter (D) and droplet height (H) when silica substrate is used. Thus, pinned triple line is observed clearly during the initial constant contact line diameter (CLD)
(Fig. 3.9a,b,c); and (5) the contact line diameter (CLD) on mica substrate also seems to have several stages even though it is not as clear as that on silica substrate (Fig. 3.9d,e,f).

![Graphs showing variations of droplet dimensions](image)

Figure 3.9. The variations of droplet dimensions according to time change, (a) silica at 1 MPa pressure and pure water during the first test, (b) silica at 1 MPa pressure and pure water during the second test, (c) silica at 1 MPa pressure and pure water during the third test, (d) mica at 5 MPa pressure and 1 molarity saline water, (e) mica at 7 MPa pressure and 1 molarity saline water, (f) mica at 10 MPa pressure and 1 molarity saline water.

When the CO$_2$ droplet size decreases, the mineral substrate-water interface has higher surface energy than others, which causes the interface to hold the triple line and the CO$_2$ droplet to be dissolved along the water-CO$_2$ interface [Lam et al., 2002a; Saghafi et al., 2014a]. Thus, when a
CO₂ droplet is initially dissolved into water, the droplet height (H) decreases while the contact line diameter (CLD) remains relatively constant, which increases contact angle. However, more CO₂ dissolution influences on the triple line slip to the direction of substrate-CO₂ interface, which causes the contact line diameter (CLD) to decrease but the contact angle to remain relatively constant. In case of mica, the heterogeneity of mica surface showed in figure 3.3 and figure 3.4 can generate more complicated pinned and slip stages of contact line diameter (CLD), which causes unclear several stages of contact line diameter (CLD) variation in the figure 3.9 [Wan et al., 2014].

3.3.2 Normalized Dimensions (CLD/H, CLD/D, and H/D)

Figure 3.10 presents three normalized dimension (i.e. CLD/H, CLD/D, and H/D) and contact angle change at different time. The ratio between droplet height and droplet diameter (H/D) remains relatively constant during tests because both droplet height (H) and droplet diameter (D) decrease together during CO₂ dissolution without the relation to pinned or unpinned triple line. Both contact line diameter (CLD) and droplet diameter (D) decrease together with the change of unpinned triple line, which cause the ratio between contact line diameter and droplet diameter (CLD/D) to be less sensitive than the ratio between contact line diameter and droplet height (CLD/H) (Fig. 3.10). CLD/H has the best agreement with contact angle among three dimensionless numbers, which is defined as a shape factor to estimate the variations of contact angle.

Figure 3.11 shows a good consistency between the contact angle and the shape factor, CLD/H (the ratio between contact line diameter and droplet height). The pinned triple line during initial CO₂ dissolution causes both contact angle and the CLD/H ratio to increase because the droplet height (H) decreases while contact line diameter (CLD) remains constant. After the triple line starts
to move, further CO\textsubscript{2} dissolution affects the decrease both the contact line diameter (CLD) and the droplet height (H), which causes contact angle and CLD/H to remain relatively constant. These relatively constant contact angles can be defined as the advancing water contact angle, which are used to explore the imbibition processing when the drained water migrates back to the CO\textsubscript{2} storage after the completion of CO\textsubscript{2} injection.

![Graphs showing variations of dimensionless numbers according to time change.](image)

Figure 3.10. The variations of dimensionless numbers according to time change, (a) silica at 1 MPa pressure and pure water during the first test, (b) silica at 1 MPa pressure and pure water during the second test, (c) silica at 1 MPa pressure and pure water during the third test, (d) mica at 5 MPa pressure and 1 molarity saline water, (e) mica at 7 MPa pressure and 1 molarity saline water, (f) mica at 10 MPa pressure and 1 molarity saline water.
Figure 3.11. The variations of shape factor (CLD/H) and contact angle according to time change, (a) silica at 1 MPa pressure and pure water during the first test, (b) silica at 1 MPa pressure and pure water during the second test, (c) silica at 1 MPa pressure and pure water during the third test, (d) mica at 5 MPa pressure and 1 molarity saline water, (e) mica at 7 MPa pressure and 1 molarity saline water, (f) mica at 10 MPa pressure and 1 molarity saline water.

While the mica substrate shows the unclear pinned and slip stages due to the heterogeneity of mica in the figure 3.9, figure 3.11 shows a clear agreement between the contact angle and the shape factor (CLD/H). While the triple line moves freely on an ideal homogeneous solid surface due to the uniform surface energy, the heterogeneity on the solid surface results in the variations of surface energy, which causes the triple line to move with the repeated pinned and slip stages.
While Wan et al. [2014] attempted to decrease the heterogeneity of mica surface through cutting the substrate with sharp scissors, blowing with air, and cleaving a fresh surface before each test, the enormous amount of contamination was observed on the mica surface that causes the contact angle on mica substrate to be ambiguous [Wan et al., 2014].

Figure 3.12 (a) presents the relations between CLD/H (or shape factor) and the contact angle. The results shows that (1) contact angle increases with CLD/H on both silica and mica substrates; and (2) mica substrate shows a larger range of CLD/H variations from 0.42 to 1.70 than silica (0.66 to 0.95), which causes the wider range of contact angle on mica substrate.

3.3.3 Droplet Volume and Shape Factor (CLD/H) Relations

Figure 3.13 presents the relations between CLD/H and droplet volume. As CO₂ droplet dissolves into water, the droplet volume continuously decreases until reaching on the solubility [Note. CO₂ dissolved in water is not able to reach on the solubility considering the volumes of one droplet and chamber size filled with the water], and droplet height (H) also continuously decreases (Fig. 3.9). However, the contact line diameter (CLD) shows two pinned and slip stages for silica (Fig. 3.9a, b, c). Silica substrate has clear pinned and slip stages. Thus, both droplet height (H) and
contact line diameter (CLD) decrease together after the pinned stage, which cause a slight increase in CLD/H with the decreased in the CO₂ droplet volume. However, mica substrate has unclear repeated pinned and slip stages (Fig. 3.9d, e, f). The contact line diameter (CLD) slightly decreases even during the slip stage while droplet height (H) continuously decreases, which causes the dramatically increases in CLD/H with the decreased droplet volume (Fig. 3.13). Also, CLD/H increased more even with the relatively constant CO₂ droplet volume after initial fast dissolution. It implies that the variations of CLD/H are not related to the change of volume when CO₂ droplet size becomes small, and the variations of contact angle depend on the heterogeneity of mineral surface, which influences on CLD/H. The result has the consistency with a previous study with coal [Saghafi et al., 2014a].

Figure 3.13. Droplet volume variations according to shape factor (CLD/H) change, a) silica substrate, b) mica substrate.

3.3.4 Heterogeneity Effects of Mineral Surface on Contact Angle Variations in Unsaturated Conditions

Figure 3.14 shows the relations between droplet volume and contact angle. As CO₂ droplet dissolves into water, the CO₂ droplet volume decreases and contact angle changes. While contact angles on silica substrate have a small range of variation like CLD/H variations according the droplet volume change; however, the contact angle on mica substrate dramatically increases with
the decreased droplet volume. It also implies that the heterogeneity of mineral surface more affect the contact angle rather than the decreased droplet volume, which has the consistency with the results by Wan et al. [2014]. Wan et al. [2014] showed that despite their effort to keep CO$_2$-saturated brine in their captive contact angle measurement set up, CO$_2$ dissolution occurred due to the unsaturated condition. They observed the pinned contact line and the droplet volume change. Wan et al. [2014] reported that the heterogeneity of mica surface and unsaturated experimental condition were reasons for uncertainty in contact angle measurement on mica substrate.

When CO$_2$ is injected into geological CO$_2$ storage in the field, CO$_2$ and brine are unsaturated conditions. Thus, both of them will be dissolved into each other until they reach on their solubility, which affect the wettability of minerals. Experimental studies showed that the contact angle changed as the result of CO$_2$ dissolution and the decreased in droplet size at unsaturated conditions [Shojai Kaveh et al., 2011; Kaveh et al., 2014; Wan et al., 2014]. Addition to the effect of CO$_2$ dissolution on contact angle, our results show that chemically heterogeneous materials like mica have the wide range of contact angle variations according to the decreased droplet volume in the figure 3.14. The extents of increased contact angle during CO$_2$ dissolution depends on the heterogeneity of mineral surface. Higher contact angles than static contact angle measured in the saturated conditions result in lower capillary pressure in the caprock, which causes the probability of leakage through sealing caprock to increase. Also, the amount of CO$_2$ disconnected bubbles in the formation becomes less than the expectation due to decreased capillary pressure. It implies that the heterogeneity of mineral surface should be considered when contact angle is selected for the prediction of the long term performance of CO$_2$ storage.
Figure 3.14. The variations of contact angle according to volume change, (a) silica at 1 MPa pressure and pure water during the first test, (b) silica at 1 MPa pressure and pure water during the second test, (c) silica at 1 MPa pressure and pure water during the third test, (d) mica at 5 MPa pressure and 1 molarity saline water, (e) mica at 7 MPa pressure and 1 molarity saline water, (f) mica at 10 MPa pressure and 1 molarity saline water.

3.4 Conclusion

This study is an attempt to understand the inconsistency among reported contact angles and to decrease the ambiguity of wettability of common minerals under geological CO₂ sequestration. The changes of mineral wettability at more practical unsaturated conditions are explored.

Experimental studies show different behaviors of contact angle change according to the droplet volume change due to CO₂ dissolution into water on silica and mica substrates. The triple
line (or contact line) with pinned and slip concepts of a droplet is introduced to explain the different behavior between silica and mica substrates.

When the CO₂ droplet size decreases, the mineral substrate-water interface holds a triple line due to higher surface energy (i.e. pinned stage), and the droplet is dissolved into water along the water-CO₂ interface. At this time, the contact angle on silica substrate increases with a small range from 34.5° to 42.1°. More CO₂ dissolution influences on the triple line slip to the direction of substrate-water interface (i.e. slip stage), which causes the contact angle to remain relatively constant. In case of mica, the heterogeneity of mica substrate surface can generate more repeated pinned and slip stages of a triple line (or contact line), which causes the contact angle dramatically to increase with more pinned stages. The variations on mica substrate are within the range of 25.4° and 68.1°.

Three dimensions of CO₂ droplet, e.g., contact line diameter (CLD), droplet height (H), and droplet diameter (D), are introduced to consider CO₂ droplet size and pinning effects on the contact angle. Three normalized dimensions (i.e. CLD/H, CLD/D, and H/D) are compared with the variation of contact angle during CO₂ dissolution. Among three ratios, CLD/H has the best agreement with the contact angle change.

While CLD/H remains relatively constant with the decreased CO₂ droplet volume on silica substrate, CLD/H continuously increases on mica substrate due to repeated pinned and slip stages. Thus, the contact angle, which has a consistency with the variation of CLD/H, depends on the heterogeneity on mineral surface rather than the droplet volume.

Increased contact angles due to the heterogeneity on mineral surface cause the capillary pressure in caprock to decrease, which results in decrease in storage capacity of CO₂. Thus, the
effect of mineral surface heterogeneity on contact angle should be considered when evaluating the long term performance of CO₂ storage.

3.5 Reference:


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Chapter 4. Variation of Contact Angles in Brine/CO₂/mica System Considering Short–term Geological CO₂ Sequestration Condition

4.1 Introduction

In recent decades, greenhouse gases including CO₂ have been considered as main contributors to climate change. Despite enormous efforts to develop clean energies such as wind and solar power, the low efficiency of these resources and excessive energy demands have made fossil fuels dependency inevitable. As a consequence, tremendous amounts of CO₂ are annually released into the atmosphere. In order to resolve the CO₂-induced problems, mitigating anthropogenic CO₂ emission is necessary. Carbon capture and storage (CCS) has been proposed as a process of capturing CO₂ from main emitters (e.g., coal-based power plants, steel and cement industrial units, oil and gas extraction industries, and so on) and then storing CO₂ safely. Among different storage forms of CO₂, geological CO₂ sequestration (GCS) has been recently suggested due to high safety and efficiency compared with other storage techniques [Bachu, 2000b; Bachu and Adams, 2003; Holloway, 2007; Benson and Cole, 2008a]. Captured CO₂ is injected and trapped in natural underground storage sites such as depleted oil/gas reservoirs, saline aquifers, deep coal seams, and deep ocean sediments for hundreds to thousand years. The main problem here is that CO₂ has lower density compared to water, causing upward migration of stored CO₂ through geo-materials as a result of buoyancy force [Iglauer, 2017]. A successful CO₂ sequestration project requires an immobilization of the injected CO₂ to prevent surface leakage or acidification of underground waters.

This immobilization is mainly conducted through four trapping mechanisms: structural, residual, solubility, and mineral trapping [Saraji et al., 2013b; Jafari et al., 2016]. Structural and residual capillary trapping mechanisms immobilize CO$_2$ in the short-term. They contribute to the safer long-term storage trapping mechanisms (i.e., solubility and mineral trapping mechanisms). For both short term mechanisms, capillary pressure plays a crucial role. In structural trapping, a layer of sealing caprock on the top of the storage site resists against upward migration of connected CO$_2$ plum by high capillary pressure, resulting in differential pressure between water and CO$_2$ in pores (Eqn. 4-1). In capillary trapping, disconnected bubbles of CO$_2$ are trapped between water in rock formation pores after drainage and imbibition processes. They are immobilized by the capillary pressure which can be calculated based on Young-Laplace equation (Eqn 4-1):

$$P_C = P_{\text{CO}_2} - P_{\text{water}} = \frac{2\gamma_{W-CO_2}\cos(\theta)}{R} \tag{4-1}$$

Where $P_C$ is capillary pressure, $P_{\text{CO}_2}$ and $P_{\text{water}}$ are pressure in CO$_2$ and water, respectively. $\gamma_{W-CO_2}$ is interfacial tension between water and CO$_2$, $\theta$ is contact angle, and $R$ is pore radius.

Contact angle, which is often used for quantifying wettability of the rocks, is an angle that can be measured between water-CO$_2$ interface and water-rock interface through water. Contact angle is the most controversial parameter influencing capillary pressure. The uncertainty observed in experimental measurement on different rocks at a wide range of GCS thermodynamics results in a high risk of leakage and low storage efficiency in GCS projects. Experimental results of wettability are very sensitive to physical and chemical properties of minerals, water quality and salinity, pressure, temperature, and the method of measurement. In spite of the efforts to control these conditions, a wide range of contact angles have been observed by different researchers. While no meaningful change in wettability with pressure has been observed for silica, calcite, and feldespar [Chalbaud et al., 2009; Espinoza and Santamarina, 2010; Bikkina, 2011; Broseta et al.,
2012; Farokhpoor et al., 2013a; Wang et al., 2013b; Saraji et al., 2014], other reports have shown that the wettability of minerals is decreased as CO₂ pressure is increased [Dickson et al., 2006; Siemons et al., 2006; Shah et al., 2008; Yang et al., 2008a; Jung and Wan, 2012; Saraji et al., 2013b]. Lower wettability means lower capillary pressure. Therefore, higher CO₂ mobility and risk of leakage are expected when the wettability is decreased.

Presence of clay in caprock requires information of contact angle values on clay surface at GCS conditions. Contact angle measurement has been conducted with a drop of water on the substrate or a bubble of CO₂ under the substrate. However, the size of clay crystals is too small (less than 2 μm) to be used as substrate [Iglauer et al., 2014]. Thus, a mica sheet is usually used as a representative of clay, especially when illite is existing in rock [Chiquet et al., 2005; Shah et al., 2008; Farokhpoor et al., 2013b]. Chiquet et al. [Chiquet et al., 2007b] have observed that the receding contact angle on mica substrate is 10°~30° at low pressure and 58°~70° at high pressure (i.e., 11 MPa). Increased pressure results in higher solubility of CO₂ in water and decreases pH of brine. Low pH neutralizes negative charges on the mica substrate, resulting in decreased repulsion force between mineral-brine and brine-CO₂ interfaces which finally causes transition of mica substrate characterization from water-wet to intermediate-wet [Chiquet et al., 2007b]. Chiquet et. al. [Chiquet et al., 2007b] have also reported that the wettability of mica substrate is more sensitive to salt concentration than quartz. While an increase in salinity from 0.1 M to 1 M of NaCl resulted in a 25° increase in drainage contact angle of the mica substrate, the wettability of quartz did not show meaningful change with changes in salinity [Chiquet et al., 2007b]. Although Chiquet et al. [Chiquet et al., 2007b] have reported significant variation in contact angle on mica substrate, others have shown negligible changes in contact angle on mica substrate. For example, Broseta et al. [Broseta et al., 2012] have reported that drainage contact angle of muscovite mica substrate is
increased less than $10^\circ$ when the pressure is increased from 0.5 MPa to 14 MPa. However, the imbibition contact angle is increased more than $30^\circ$ [Broseta et al., 2012]. Such discrepancy in published contact angles on mica substrate might be due to the following: (1) imperfection of mica surface including physical and chemical faults at the beginning of experiments, (2) altering mica surface during experiments that results in impurity on mica surface, (3) dissolution of CO$_2$ bubble due to hardship in providing saturated condition, (4) duration, number, and sequence difference of CO$_2$ and water contact with mica surface [Wan et al., 2014].

Contact angle at unsaturated conditions should be considered because aquifer formation is not saturated when CO$_2$ is introduced into storage sites. This can lead to CO$_2$ dissolution into the aqueous phase. In addition, solubility of CO$_2$ in brine varies with changing thermodynamics of storage sites such as the temperature, pressure, and salinity. This can result in unsaturated conditions at storage sites [Spycher et al., 2003; Lagneau et al., 2005; Sypcher and Pruess, 2010]. Thus, the wettability behavior in the presence of CO$_2$ at unsaturated conditions has been studied [Siemons et al., 2006; Yang et al., 2008a; Saghafi et al., 2014a; Jafari and Jung, 2016]. For example, Saghafi et al. [Saghafi et al., 2014a] have observed that the contact angle on a coal surface is increased with time during CO$_2$ dissolution into water. They called the increasing time-dependent contact angle as a transient receding contact angle. Yang et al. [Yang et al., 2008a] have measured contact angle with a brine droplet on a rock surface in a chamber filled with CO$_2$. The brine droplet was spread onto the rock surface during CO$_2$ dissolution into the brine, causing a contact angle change. This was called as dynamic contact angle due to the advancing contact line of the brine droplet. When brine spreading was completed and the length of contact line became constant, contact angle was called an equilibrium contact angle in their study.
Recently, Shojai Kaveh et al. [Kaveh et al., 2014] have clarified two clear regimes of contact angle change on coal and sandstone at unsaturated conditions: 1) contact angle is increased during CO$_2$ dissolution; and 2) contact angle is constant during CO$_2$ diffusion. Jafari and Jung [Jafari and Jung, 2016] have observed the change of contact angle on a silica and mica surface at unsaturated conditions, monitored CO$_2$ bubble dimensions change with time due to dissolution, and suggested a shape factor that represents the ratio of contact line to the height of bubble at apex. The contact line is the diameter of CO$_2$ bubble contacting with solid surface. When the size of a CO$_2$ bubble is small enough to neglect gravity, heterogeneity of the surface plays the most important role in the shape of the bubble and contact angle variation with time [Jafari and Jung, 2016].

While previous studies with a silica have been conducted at various conditions such as pressure, temperature, and salinity, only one type of mica substrate has been used at limited conditions [Jafari and Jung, 2016]. Thus, more studies are needed to clarify changes in contact angle on mica substrate at unsaturated condition over a wide range of pressures relevant to geological CO$_2$ storage sites. The objective of the present study is to explore the variation of contact angle on mica sheet using a captive bubble method at a wide range of pressures with different salinities.

### 4.2 Materials and Methods

#### 4.2.1 Materials

Two types of muscovite mica substrates, V1 and V5 (Electron Microscopy Sciences), were used for this study. Figure 4.1 shows an atomic force microscopy (AFM) image used to measure the roughness of an area of 50 $\mu$m $\times$ 50 $\mu$m for the two mica substrates. The roughness of mica
surface was measured twice. Average roughness values for mica V1 and V5 types were 0.192 ± 0.013 and 0.218 ± 0.018 nm, respectively. Isopropyl alcohol (70%) and deionized water (DI) was used to clean mica substrates before each test. Substrates were carried and placed for tests with gloves and tweezers to avoid unexpected contamination. Also, they were used only once for each test to ensure reproducibility of experiments. For the fluids, brine with various NaCl molarities (i.e., 0.1, 1, and 3 M) and CO₂ with 99.99% purity were prepared.

![AFM image for an area of 50 µm×50 µm. (a) Mica type V1, (b) Mica type V5. AFM: atomic force microscopy.](image)

**4.2.2 Experimental Set-up**

A captive bubble method was used to measure contact angles. A high-pressure stainless steel chamber with ~20 MPa capacity was designed to allow monitoring the evolution of CO₂ droplet on the substrates during tests through glass windows. A precise high-pressure syringe pump (Teledyne ISCO, 500 HP) was connected to the high-pressure stainless steel chamber to provide target pressure. A high-resolution camera (16.2 Mega Pixel, Nikon D5100) was used to capture images of CO₂ bubbles. Time-lapse pictures were analyzed with an image processing software (ImageJ) to measure contact angles. Average values of the left and right
contact angles on CO$_2$ bubbles are reported. Differences between left and right contact angle values were mostly less than 0.5°. Temperature remained constant at 318 ± 1 K. Pressure transducer and thermocouple connected to a data logger were used to monitor pressure and temperature variations, respectively, during tests. Schematic design of the experiment set-up and further details have been described by Jafari and Jung [Jafari and Jung, 2016].

4.2.3 Experimental Procedure

The high pressure chamber was filled with deionized water (DI) or brine. The high-pressure syringe pump filled with CO$_2$ was connected to the top of the chamber and pressurized up to 1 MPa with CO$_2$. The chamber was kept for 24 hours under the pressure and constant temperature of 318 ± 1 K to allow water to be partially saturated with CO$_2$. The pressure was increased up to 3 MPa. Then a CO$_2$ bubble was injected through a needle attached to the bottom of the chamber. The CO$_2$ bubble was placed under a mica substrate. It started to dissolve into deionized water (or brine) because deionized water (or brine) was not fully saturated. A camera was used to monitor the evolution of CO$_2$ bubble every 2 sec until the bubble shrinks in a small size that contact angle could be not measured anymore. The available set-up is not able to detect contact angle when the volume of CO$_2$ bubble is less than 0.15 mm$^3$. After CO$_2$ bubble disappeared, pressure was increased up to next target value (i.e., 5 MPa). Then another CO$_2$ bubble formed under the mica substrate and was monitored with the camera again. This was repeated at different pressures (i.e., 7, 10, and 13 MPa) and various salinities (0, 1, and 3 Molar NaCl). After completing each test, the chamber was depressurized, dismantled, and completely cleaned for the next test with another mica substrate or salinity.
4.3 Results and Discussion

In the present chapter, the measured contact angle is considered as static contact angle. Although the triple line has a motion during dissolution, it is too slow to be recognize as dynamic contact angle, because the dynamic parameters appear for capillary numbers higher than $10^{-4}$ (capillary number is ratio of viscous forces to interfacial forces of surface and show the dominancy of these forces). Such high capillary numbers is typically observed when the triple line motion on solid is faster than 0.1 mm/s [Katoh et al., 2015]. The rate of triple line movement on the substrate due to the shrinkage of bubble is much less than this number for all the tests.

On the other hand, we avoid to call the measured contact angle as equilibrium contact angle as well. The stable equilibrium contact angle is only achieved in a global minimum free energy configuration on an ideal solid surface under perfect laboratory condition. In the literature, what simply called “equilibrium contact angle” is indeed a local minimum free energy configuration of the system or a meta-stable equilibrium contact angle [Ruiz-Cabello et al., 2014]. Such equilibrium contact angle is usually measured when the fluids are fully saturated.

Also, to be clear on definitions in this study, the measured contact angle immediately after introducing CO$_2$ is called initial contact angle. The initial volume of bubble mostly ranges between 30 to 10 mm$^3$. The value of contact angle is named final, when due to dissolution the bubble size decreases to a value (volume $< 0.15$ mm$^3$) that measuring contact angle is not possible with available set-up. The word “final” here implies the final measurement, not the end of dissolution or reaching equilibrium, because dissolution will progress until the bubble become disappeared.
4.3.1 Variation of Contact Angle with Time

Figure 4.2 shows variation of contact angle with time on mica surfaces (types V1 and V5) at several pressures and salinities (i.e., 3~13 MPa and 0~3 M NaCl). While it is difficult to explore the effect of pressure, surface roughness, and salinity on contact angle by the figure 4.2, contact angles is generally increasing with time for all tests, consistent with results of previous studies [Siemons et al., 2006; Kaveh et al., 2014; Saghafi et al., 2014a].

![Figure 4.2](image)

Figure 4.2. Contact angle change with time on mica substrate. (a) Type V5 with deionized water, (b) Type V1 with deionized water, (c) Type V5 with 1 M NaCl, (d) Type V1 with 1 M NaCl, (e) Type V5 with 3 M NaCl, (f) Type V1 with 3 M NaCl.
After the CO₂ bubble is introduced into the aqueous phase (i.e., deionized water or brine)-filled chamber, CO₂ bubble size was decreased due to CO₂ dissolution into the fluid until it disappeared or when it became too small to be recognized with the camera. At the same time, the contact angle increased with decreasing CO₂ bubble size.

In literature, a dimensionless Bond number $Bo$ is usually defined considering gravity force and interfacial tension that could influence droplet shape and contact angle (Eqn 4-2) [Kaveh et al., 2014].

$$Bo = \frac{\Delta \rho g L^2}{\gamma_{lg}}$$  

where $Bo$ is a dimensionless Bond number, $\Delta \rho$ is the density difference between liquid and gas, $L$ is a characteristic length equals to the diameter of a liquid droplet (or a gas bubble), and $\gamma_{lg}$ is interfacial tension between liquid and gas phases.

Bond number decreases by progress of dissolution. Shojai Kaveh et al. [Kaveh et al., 2014] have observed that contact angles on a sandstone increases as the Bond number decreases up to 0.9 and then it relatively remains constant when the Bond number is smaller than 0.9 [Kaveh et al., 2014]. In the present study, although dimensionless Bond number $Bo$ is within the range of 0.006~0.482, contact angle increased with decreasing size of CO₂ bubble. This implies that changes in contact angle on mica substrates are not related to dimensionless Bond number $Bo$ considering CO₂ dissolution. Such changes might be due to other factors such as heterogeneity of mica surface.

Jung and Wan [Jung and Wan, 2012] have shown that the contact angle on silica surface is increased within a range of 7 ~ 10 MPa. However, it remains constant at pressure greater than 10 MPa. However, figure 4.2 does not show any clear trend of contact angle according to the changes in pressure. Mostly, the increase in contact angle at higher pressure (i.e. 10 MPa and 13
MPa) with time is less than that at lower pressure because of stepwise pressurization in each test. Considering figure 4.2d, after completion of the test with V1 type mica substrate at pressure of 3 MPa, the pressure is increased to 5 MPa and new CO$_2$ bubble forms under the same mica substrate. The evolution of CO$_2$ bubble is monitored with the camera. This is repeated with higher pressure (i.e., 7 MPa, 10 MPa, and 13 MPa). This implies that more amount of CO$_2$ can have already dissolved in the water/brine when the pressure reached to a higher pressure such as 13 MPa. Thus, the dissolution rate of CO$_2$ bubble is decreased with increasing pressure. This might have caused the contact angle to increase less with time at higher pressures as shown in the figure 4.2.

4.3.2 Changes in Contact Angle During CO$_2$ Dissolution

Figure 4.3 shows initial- and final- contact angles at different pressures. These are the first- and the last- contact angles of each test case from the figure 4.2. Results shows that most initial contact angles is slightly increased with increasing pressure which can be due to decreased pH during CO$_2$ dissolution into water/brine. A distinct correlation between initial contact angle and pressure has not been observed in some previous studies, including experimental results with coal [Siemons et al., 2006; Yang et al., 2008a], experiments with mica at saturated condition [Wan et al., 2014], experiments with silica and calcite at 20 °C temperature and 20 MPa pressure [Espinoza and Santamarina, 2010], receding contact angle of mica and calcite [Broseta et al., 2012], and contact angle with quartz, feldspar and calcite [Farokhpoor et al., 2013b]. However, other reports have shown that dynamic contact angle on mica has been increased considerably with pressure [Chiquet et al., 2007b; Shah et al., 2008; Broseta et al., 2012; Arif et al., 2016b]. Thus, the effect of pressure on contact angle change remains unclear on the grounds that the observed
inconsistency in previous studies, including results of this study. Although final contact angle shows a slight increase with pressure in this study (Fig. 4.3), a clear trend is not observed.

![Graphs showing variations of initial and final contact angles with pressure. Each graph represents a different condition: (a) Type V5 with deionized water, (b) Type V1 with deionized water, (c) Type V5 with 1 M NaCl, (d) Type V1 with 1 M NaCl, (e) Type V5 with 3 M NaCl, and (f) Type V1 with 3 M NaCl.]

Figure 4.3. Variations of initial- and final- contact angles with pressure. (a) Type V5 with deionized water, (b) Type V1 with deionized water, (c) Type V5 with 1 M NaCl, (d) Type V1 with 1 M NaCl, (e) Type V5 with 3 M NaCl, (f) Type V1 with 3 M NaCl.

All final contact angles are higher than initial contact angles at each experimental condition (Fig. 4.3). Comparing mica with silica, Jafari and Jung [Jafari and Jung, 2016] have shown that heterogeneity of mica substrate has more impact on the contact angle change than the decrease in
CO$_2$ bubble volume [Jafari and Jung, 2016]. Considering the fact that Bond number values of initial bubbles are less than 0.5, the bubble size change effect on contact angle diminishes and the role of heterogeneity of mica surface can have more influence on the change of contact angle in this study. Thus, changes in CO$_2$ bubble volume and heterogeneity of mica surface should be considered together to explain the increased contact angle during CO$_2$ dissolution.

Figure 4.4 shows differences between final- and initial- contact angles. The difference increases when pressure increases from 3 MPa to 5 MPa or 7MPa, but it decreases at high pressures (i.e., 10 and 13 MPa). Our experiments starts at the pressure of 3 MPa in each test. The pressure is then stepwise increased to the next target pressure. CO$_2$ solubility is increased with pressure, which causes CO$_2$ bubble to dissolve faster into the water/brine. Thus, final contact angles increases at pressure of 5MPa or 7MPa. However, because of introducing more number of bubbles in the used stepwise method, more amounts of CO$_2$ has already been dissolved into the water/brine before the high pressure (i.e., 10 and 13 MPa) tests are started. Thus, CO$_2$ dissolution rate is decreased at higher pressure in our tests, which decelerated changes in CO$_2$ bubble size, causing less increase of contact angle during a stick stage (or pinning effect). This is in good agreement with results of a previous study showing that changes in unsaturated contact angle are lower at higher pressures (12 MPa) [Yang et al., 2008a].

Triple line (or contact line) is defined as the line where three phases of solid substrate, liquid, and gas are in contact altogether [Tadmor, 2004; Wan et al., 2014; Jafari and Jung, 2016]. The triple line is moving when CO$_2$ bubble is dissolved into the aqueous phase. This is called a slip stage. At this moment, contact angle remains relatively constant.
Figure 4.4. Difference in final- and initial- contact angle. (a) Type V5 with deionized water, (b) Type V1 with deionized water, (c) Type V5 with 1 M NaCl, (d) Type V1 with 1 M NaCl, (e) Type V5 with 3 M NaCl, (f) Type V1 with 3 M NaCl.

However, when the triple line meets a surface spot with higher surface energy, the movement of triple line stops and the water-CO\(_2\) interface is dissolved into the water/brine without further movement of the triple line. This is called as a stick stage or a pinning effect causing contact angle to increase rapidly during CO\(_2\) dissolution [Jafari and Jung, 2016]. A dimensionless number (CLD/H) called shape factor, which is defined as the ratio of triple line diameter (CLD) to the...
height of CO₂ bubble at apex (H), has a good agreement with contact angle changes during CO₂
dissolution when slip-stick stages are observed [Saghaei et al., 2014a; Jafari and Jung, 2016]. The
irregular trends of contact angle change with pressure in this study could be explained by
complicated slip and stick stages (or pinning effect) of heterogeneous mica surface [Jafari and
Jung, 2016]. Figure 4.5 shows both initial and final contact angles and dimensionless numbers
(CLD/H) at different pressures. There is a consistency between contact angels and CLD/H, proving
the validity of dimensionless number (CLD/H). This implies that changes in contact angle on mica
surface are affected by complicated slip and stick stages (or pinned effect) during CO₂ dissolution
at unsaturated conditions.

4.3.3 Effect of Salinity on Contact Angle

Figure 4.6 shows changes in initial- and final- contact angles with salinity (NaCl) in the
range of 0 to 3M. Results shows unclear trend between contact angles and increasing salinity.
While equilibrium contact angle on silica substrate has been reported to be increased with salinity
(i.e., with a net increase of 19.6°±2.1° at 5.0 M NaCl) [Jung and Wan, 2012], the relation between
contact angle on mica substrate and salinity has not been clearly observed in other studies [Broseta
et al., 2012; Wan et al., 2014]. Although Chiquet et al. [Chiquet et al., 2007b] have observed an
increase of about 25° in contact angle with increasing salinity from 0.1 M to 1 M, they have stated
that the increase in contact angle with salinity might be due to poor reproducibility of contact
angle measurement using a needle with a large diameter of droplet. Recently, Arif et al. [Arif et
al., 2016c] and [Arif et al., 2016a] have shown that both advancing and receding contact angles on
mica substrate are increased with salinity. This has been explained by the decrease in negative
charge of mica surface due to strong shield of cations in saline water [Kaya and Yukselen, 2005;
Adamczyk et al., 2010; Saraji et al., 2013a; Arif et al., 2016c]. Considering the inconsistency
between equilibrium and advancing/receding contact angles, further studies are needed to determine contact angles on mica surface with a variety of salinities.

Figure 4.5. Variations in contact angle and dimensionless number (CLD/H) at various pressure. (a) Type V5 with deionized water, (b) Type V1 with deionized water, (c) Type V5 with 1 M NaCl, (d) Type V1 with 1 M NaCl, (e) Type V5 with 3 M NaCl, (f) Type V1 with 3 M NaCl.

Figure 4.6 shows that final contact angles versus salinity are more scattered than initial contact angles. Initial contact angles are measured at the start of CO₂ dissolution. However, final contact angles are measured when dissolution is progressing until camera could not recognize CO₂ bubble due to small sizes. Therefore, at the time of measuring final contact angle, there is enough
time for the triple line to contact with different spots with various surface energy on the solid surface and formation of slip-stick regimes. Compared to salinity, heterogeneity on mica surface might have more influence on the change of contact angle due to pinning effect during CO\textsubscript{2} dissolution.

Figure 4.6. Variations in contact angle with salinity. (a) Initial contact angle on mica V5, (b) Final contact angle on mica V5, (c) Initial contact angle on mica V1, (d) Final contact angle on mica V1.

4.3.4 Comparing Contact Angles on Mica Surface at Unsaturated Conditions with Advancing/Receding/Equilibrium Contact Angles

Figure 4.7 shows contact angles on mica surface measured in this study as well as all types of contact angles (i.e., advancing, receding, and equilibrium contact angles) compiled from previous studies [Chiquet et al., 2007b; Mills et al., 2011; Broseta et al., 2012; Farokhpoor et al.,
As it is already discussed, the measured contact angle in this study is not dynamic. However, the objective of this comparison is to compare the measured static contact angle under influence of unsaturated condition with receding and advancing contact angles, which are widely considered in literature as the lower and upper boundary of contact angle, respectively. Results shows the following: (1) all compiled contact angles have a wide range of values on mica surface due to heterogeneous nature of mica surface and different experimental procedures, (2) advancing contact angles are higher than receding contact angles while equilibrium contact angles lie between advancing- and receding-contact angles, (3) initial contact angles in this study are within the range of receding contact angles in previous studies, and (4) final contact angles in this study are within the range of advancing contact angles reported in previous research studies. Considering Young’s equation, contact angle must be unique on a smooth and homogeneous material surface. However, the heterogeneity on mica surface can influence complicated slip/stick stages during CO$_2$ dissolution at unsaturated condition. This can increase contact angle, resulting in a wide range of values [Jafari and Jung, 2016]. While initial contact angle were within the range of receding contact angles (lower boundary of contact angles), increased final contact angles during CO$_2$ dissolution were similar to advancing contact angles (upper boundary of contact angle) (Fig. 4.5). As a consequence, increased contact angle caused capillary pressure to decrease, which influences the migration of disconnected CO$_2$ bubble after CO$_2$ injection and the interconnection of them in aquifer sites. In addition, breakthrough capillary pressure in caprock can be decreased when CO$_2$ meets unsaturated water in caprock, resulting in CO$_2$ leakage through the caprock.
4.3.5 Contact Angles at Unsaturated Conditions

Figure 4.8 shows both initial- and final- contact angles measured in this study as well as compiled contact angles on various materials (i.e., coal, sandstone, and silica) at unsaturated conditions in previous studies. Results show that: (1) contact angles on coal surface are within a wide range of 40°~80° at the initial stage and 90°~140° at the final stage because coals surface consists of various organic and mineral materials with different surface energies, resulting in high heterogeneity [Drelich et al., 1997; Gosiewska et al., 2002]; (2) increased contact angles on silica surface from initial- (30°~35°) to final- stages (35°~45°) is less than those on coal surface. Silica surface with lower chemical heterogeneity and roughness allows the triple line to slide easily and
limits the pinning effect, thus more repeatability has been observed for contact angle on silica (glass) surface, resulting in less change of contact angle \cite{Saghafi et al., 2014a};

(3) changes in contact angle on mica surface during CO\textsubscript{2} dissolution are between those of silica and coal surface \cite{Wang et al., 2013a}; and (4) the range of contact angle on type V5 mica surface was similar to that on type V1 (i.e., 25° ~ 90° on type V1, and 25° ~ 90° on type V5) even though type V5 had relatively higher roughness than type V1 (Fig. 4.1).
Previous studies conducted under saturated condition have shown that contact angle does not increase with roughness. Even in some experiments, the highest hysteresis of contact angle has been observed on material surface with intermediate roughness [Johnson and Dettre, 1964; Chiquet et al., 2007b]. At unsaturated condition, it seems that chemical and physical heterogeneity (roughness) are dominant in hysteresis as they can increase the probability of a pinned triple line [Jafari and Jung, 2016].

4.3.6 Capillary Pressure Change with Depth

Invasion of non-wetting fluid (CO₂) into caprock is the main concern for any geological CO₂ sequestration projects. It is usually estimated by measuring CO₂ breakthrough capillary pressure with Young-Laplace equation (Eqn 4-1) [Li et al., 2005], thus this estimation needs determination of all effective parameters in the equation 4-1 as below:

Wettability: as shown earlier, mica is not completely water-wet. This study also showed that the wettability on surface substrate could change during dissolution of CO₂ into aqueous phase (water or brine) when unsaturated CO₂ is injected into aquifer sites. Expected capillary pressure change during CO₂ dissolution in CO₂ storage is calculated by measured initial and final contact angle values shown in the figure 4.3.

Pore throat size: finding a proper pore throat size of percolating path is also of importance for a realistic estimation of capacity and safety. The pore throat size that governs breakthrough capillary pressure is called critical pore diameter. It is defined as the minimum diameter along the percolating path [Espinoza and Santamarina, 2010]. Effective stress, which increases with depth, can change the structure of granular materials or rocks and affect pore sizes as well.
Espinoza and Santamarina [Espinoza and Santamarina, 2010] have estimated the critical pore size based on Horseman et al. [Horseman et al., 1999]’s experimental works on bentonite blocks under different effective stresses. To calculate pore size in different depths (different effective stresses) in this study, a power expression is proposed based on calculated pore size by Espinoza and Santamarina [Espinoza and Santamarina, 2010] in the equation (4-3):

\[ d = 260.22 \ p^{-0.913} \tag{4-3} \]

where \( d \) is critical pore diameter (nm) and \( p \) is effective pressure (MPa) equal to hydrostatic pressure changing with depth.

Interfacial tension: lower discrepancy are observed for interfacial tension among measured values under geological sequestration by different researchers. Here, the interfacial tension between CO\(_2\)-water (or brine) has been selected from the experimental study by [Bachu and Bennion, 2009].

Pore throat diameter and interfacial tension used in calculating capillary pressure under different effective stress or depths are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Pore diameter (nm)</th>
<th>Interfacial tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Salinity (0 M)</td>
</tr>
<tr>
<td>3</td>
<td>95</td>
<td>54.1</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>38.1</td>
</tr>
<tr>
<td>7</td>
<td>44</td>
<td>30.9</td>
</tr>
<tr>
<td>10</td>
<td>32</td>
<td>24.2</td>
</tr>
<tr>
<td>13</td>
<td>25</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: The brine in the present work was made of water and NaCl. However, the brine used in the study by Bachu and Bennion [Bachu and Bennion, 2009] was made of several types of ions.

Table 4.1 shows that both interfacial tension and pore diameter size are decreased as pressure (or depth) is increased. While interfacial tension causes capillary pressure to decrease, the
decrease of pore diameter size results in increase of the capillary pressure. The breakthrough capillary pressure calculated is presented in the figure 4.9.

Figure 4.9 shows that initial capillary pressure generally increased slightly with depth. Injected CO$_2$ is dissolved with time. Contact angle is increased, causing capillary pressure to decrease. This implies that breakthrough capillary pressure is critically decreased during CO$_2$ dissolution and leakage probability is increased with time. In case of V5 type mica substrate at 3M salinity, the capillary pressure was less than zero in the figure 4.9e. This could result in CO$_2$ leakage through penetration into pores.

It is complicated to implement these results for a practical geological CO$_2$ problem. There is a simplification here (and in many conducted related studies) in the geometry of the fluids interface and solid substrate in comparison with the complicated morphology of pores inside a rock. Although mica substrate is discussed in this study as a heterogeneous material in several parts of this study, it is quiet homogenous and smooth in relation to surface of a rock pores. Besides, the exact mechanism of the dissolution in terms of diffusion of CO$_2$ and changing the condition from unsaturated to saturate in the fluids exposed to injection front and the time scale for having unsaturated condition needs further study.
Figure 4.9. Capillary pressure with depth. (a) Type V5 with deionized water, (b) Type V1 with deionized water, (c) Type V5 with 1 M NaCl, (d) Type V1 with 1 M NaCl, (e) Type V5 with 3 M NaCl, (f) Type V1 with 3 M NaCl.

4.4 Conclusion

A series of contact angle measurements by captive bubble method were performed for two types of mica substrates (i.e., types V1 and V5) to explore the wettability behavior considering unsaturated water/brine for geological CO$_2$ sequestration in aquifer sites. In order to simulate unsaturated condition in storage sites, fresh CO$_2$ bubble was introduced into an unsaturated
Results of this study are summarized as below: 1) CO$_2$ bubble is dissolved into water/brine, causing contact angle on mica surface to increase with time; 2) Variations in contact angle with time are compared using two dimensionless numbers (dimensionless Bond number $B_o$ and shape factor CLD/H). It can be concluded that heterogeneity on mica surface has more influence on the change of contact angle during CO$_2$ dissolution than decreased CO$_2$ bubble size and gravity/buoyancy effect. Thus, the extent of contact angle change on mica surface with high heterogeneity on the surface is much more than that on silica surface with relatively homogeneous surface. Salinity does not show a clear impact on contact angle on mica surface due to heterogeneity. In addition, shape factor (CLD/H) is validated to have a good agreement with contact angle at unsaturated conditions. 3) The contact angles measured by previous studies were compared with the initial- and final- contact angles measured in this study, which are the contact angles of the bubble immediately after introducing and the last detectable bubble before complete dissolution, respectively. Advancing contact angles are higher than receding contact angles while equilibrium contact angles are located between advancing- and receding- contact angles. Initial- and final- contact angles on mica surface are placed within the range of receding- and advancing- contact angles, respectively. 4) A dramatic decrease of capillary pressure in sealing caprock layers in CO$_2$ storage sites is expected when fresh CO$_2$ is injected considering changes in contact angles from initial- to final- contact angles with time. This implies higher possibility of CO$_2$ leakage due to decreased CO$_2$ breakthrough capillary pressure.

4.5 Reference:


Bachu, S., and D. B. Bennion (2009), Interfacial tension between CO2, freshwater, and brine in the range of pressure from (2 to 27) MPa, temperature from (20 to 125) °C, and water salinity from (0 to 334 000) mg · L$^{-1}$, *J. Chem. Eng. Data*, 54(3), 765–775, doi:10.1021/je800529x.


doi:10.1021/la0527238.


Shah, V., D. Broseta, and G. Mouronval (2008), Capillary Alteration of Caprocks by Acid Gases,


Wang, S., Z. Tao, S. M. Persily, A. F. Clarens, E. Engineering, T. Hall, and M. Road (2013a), CO2 Adhesion on Hydrated Mineral Surfaces,


Chapter 5. Direct Measurement of Static and Dynamic Contact Angles Using a Random Micromodel Considering Geological CO₂ Sequestration

5.1 Introduction

Despite all the efforts towards developing renewable energy, fossil fuels are still the main source of energy. CO₂ emission is an inevitable consequence of fossil fuel combustion. Geological CO₂ sequestration has been recently developed as a promising method to decrease anthropogenic CO₂ emission. The main idea of this method is to separate CO₂ (i.e., CO₂ from other gases in main emitters such as fossil fuel-based power plants and other industrial units), transfer it by pipelines or tanks, and finally inject it into underground layers such as depleted oil and gas reservoirs, deep saline aquifers, deep unmineable coal beds, and methane hydrate bearing sediments. This injected CO₂ is trapped underground by two short-term mechanisms: structural trapping and capillary (or residual) trapping. In the long-term, two safer mechanisms, solubility trapping and mineral trapping, are activated to trap CO₂ underground [Bachu, 2000b; Benson et al., 2005; Benson and Cole, 2008a; Wildenschild et al., 2011; Jafari et al., 2016]. The two short-term mechanisms are highly important. They are the focus of this work because they guarantee prompt safety of storage. In addition, they can trigger the safer long-term mechanisms.

Capillary force is the main factor governing the multiphase flow in porous media along with viscous and inertial forces. Connected CO₂ plume is trapped under a sealing caprock by capillary pressure during structural trapping. Disconnected CO₂ bubbles are immobilized among rock pores by water/brine for residual trapping as a result of hysteresis and local capillary trapping [Krevor et al., 2015a].

This chapter was previously published as Jafari, M., Jung, J. (2017). “Direct measurement of static and dynamic contact angles using a random micromodel considering geological CO₂ sequestration” Sustainability, 9(12), 2352.
Capillary or residual trapping is the more favorable mechanism between the abovementioned two short-term storage trappings. In structural trapping, a pileup and thick layer of connected CO\textsubscript{2} causes an enormous uplift pressure under a sealing caprock. Any phenomenon affecting the integrity of the sealing caprock layer can dramatically increase the risk of an abrupt leakage. However, in capillary (or residual) trapping, disconnected bubbles of CO\textsubscript{2} are immobilized in a distributed form in rock pores by local capillary pressure difference. Thus, capillary (or residual) trapping is much safer than structural trapping. Also, capillary trapping provides more chance for disconnected CO\textsubscript{2} bubbles to be dissolved into water/brine, consequently increasing the rate of mineral trapping [Kimbrel et al., 2015]. The Inter-governmental Panel on Climate Change (IPCC) has also emphasized the importance of capillary (or residual) trapping for safe and economical geological CO\textsubscript{2} storage [IPCC, 2005].

Wettability is the most crucial factor among various parameters affecting capillary pressure because of its complexity and uncertainty. Wettability is often quantified by measurement of contact angle which is the angle between the water–CO\textsubscript{2} interface and rock surface measured through the denser phase (water here). The contact angle can be categorized into different types. If the water–CO\textsubscript{2} interface has no motion, the contact angle is called a static contact angle. A dynamic contact angle is measured when the interface has a motion on the solid (i.e., rock or soil) surface and is categorized as receding and advancing based on the direction of the fluids interface.

Any value of the abovementioned contact angle should be considered in a CO\textsubscript{2} storage process. For example, when CO\textsubscript{2} pushes water during initial injection, a receding contact angle should be considered. When some portion of CO\textsubscript{2} with density lower than water migrates upward and reaches under caprock and tends to penetrate into the sealing caprock, a receding contact angle should be considered. After completing CO\textsubscript{2} injection, water imbibes into the CO\textsubscript{2} storage by pressure
rearrangement which traps some portion of CO$_2$ as the form of disconnected bubbles. Each side of the CO$_2$ bubble is under advancing or receding condition depending on the direction of bubble motion. Contact angle is under static condition when the motion of the CO$_2$ bubble stops.

The pore-scale numerical model of fluids flow provides considerable information, such as fluid configuration during and after injection, capillary breakthrough pressure, and relative permeability. These can be applied to estimate the capacity and safety of a storage. A robust pore-scale numerical model requires knowledge of in situ contact angle in different modes. However, previous models suffer uncertainty originating from the lack of a direct contact angle measurement inside pores [Scanziani et al., 2017]. Technical drawbacks have inhibited researchers from measuring the contact angle inside a rock pore directly. For many years, contact angles have been measured indirectly using methods such as capillary rise or pressure measurements using a capillary tube or thin plate filled with powder or bids of a certain material based on Lucas–Washburn and Young–Laplace equations, capillary pressure curves, USBM (United States Bureau of Mines), or Amott methods [Amott, 1958; Donaldson et al., 1969; Kwok et al., 1995; Labajos-Broncano et al., 2001; Alghunaim and Zhang Newby, 2016; Alghunaim et al., 2016; Herring et al., 2016; Liu et al., 2016]. These indirect methods only yielded a statistical sense of microscopic behavior of rock or soil samples. Values of in-situ contact angles and local capillary pressure are not distinguishable [Scanziani et al., 2017]. In a different approach, static and dynamic contact angles have been vastly measured on a flat surface representing a specific mineral surface (i.e., silica, mica, or natural rock) using various methods such as sessile drop, captive bubble, Wilhelmy plate, and dual-drop dual-crystal (DDDC) methods [Rao and Girard, 1996; Ramé, 1997; Kwok and Neumann, 1999; Chiquet et al., 2005, 2007b; Bikkina, 2011; Broseta et al., 2012; Saghafi et al., 2014a; Wan et al., 2014; Li and Fan, 2015; Jafari and Jung, 2016; Jung and Hu, 2016].
High discrepancies in contact angles measured in literature have been observed. This is caused by the use of different measurement methods, rock or mineral surface imperfections, and surface cleaning methods [Wan et al., 2014]. Whether the contact angle on a flat surface can properly represent wettability inside of a porous medium pore has been a great concern. Microscopic roughness and chemical heterogeneity of pore walls originate from different in-situ minerals and curvature of pore walls, making the contact angle measured on a smooth flat surface an unreliable one for pores inside porous media [Khishvand et al., 2016].

Lin et al. [Lin et al., 2015] had shown a good agreement between receding contact angles both on a flat surface and inside a capillary tube for very smooth polymers. However, Li et al. [Li et al., 2014] have recently reported that water contact angle on a flat glass sheet can be different from a contact angle inside of a capillary tube with the same material (the inner diameter of the tube ranged from 100 to 1000 μm). The importance of more realistic wettability in predicting multiphase flow behavior requires the development of new techniques for measuring contact angle at pore-scale level. The recent X-ray computed tomography (micro-CT) method has provided a powerful tool to study pore and micro-scale characterization of rocks and multiphase fluid flow mechanisms, including pore structure morphology and local capillary pressure measurement [Wildenschild and Sheppard, 2013; Andrew et al., 2014a, 2014c; Armstrong et al., 2014; Lv et al., 2017]. Using the micro-CT technique, it is really difficult to measure dynamic contact angles due to the slow imaging process [Khishvand et al., 2016]. Thus, static contact angles have been measured with rocks, sand packs, and glass bids, showing a wide range of contact angles at pore level. The wide range of static contact angles are due to the following: (1) pore topology, hysteresis, surface chemical and physical heterogeneity, and injection patterns (i.e., drainage and imbibition) [Andrew et al., 2014b; Khishvand et al., 2016; Klise et al., 2016; Lv et al., 2016, 2017;
Scanziani et al., 2017); (2) relaxation of contact angle [Khishvand et al., 2016]; and (3) low resolution of images. Thus, Scanziani et al. [Scanziani et al., 2017] have proposed an “effective contact angle” measurement using fluid–fluid interface curvature instead of “true contact angle” at the contact line of fluids and rock surface. When CO₂ injection is stopped, the movement of the CO₂ interface front stops and a static contact angle can be measured. At this moment, the interface is approaching an equilibrium condition called the relaxation of contact angle [Khishvand et al., 2016].

In present study, considering in-situ CO₂ flow in porous media, contact angles are directly measured inside pores using a high-pressure micromodel with random pore network pattern. The transparent micromodel provides high resolution observation of fluids interface, and imaging is fast enough to capture dynamic contact angle. To the best of the authors’ knowledge, it is the first pore-scale dynamic contact angle measurement when the interface of the fluids is moving inside the channels of a randomly pattern micromodel. Moreover, the preferential behavior of wetting and non-wetting fluids in occupying different pores and throat size is also observed by the used micromodel which is not achievable with capillary tube measurement. This study is an effort to determine the effect of pore size on wettability in a micromodel with relatively homogenous material and simple geometry in comparison with a real rock core. The results of this study can provide valuable information regarding pore-scale wettability behavior of porous media that can be applied in simulation of two-phase immiscible fluid flow for geological CO₂ sequestration or other projects involved with injection of CO₂ underground.
5.2 Materials and Methods

5.2.1 Micromodel

High-pressure microchips (Micronit Microfluidics, Enschede, Netherlands) with a random network as a micromodel is used (Fig. 5.1). These microchips are made of a borosilicate glass with a network dimension of 20 × 10 mm encompassed in a polymer (PP) cartridge with dimension of 75 × 25 mm. The micromodel consists of two layers of glass with thickness of 1100 and 700 μm. One of these layers is etched with a random pattern of square channels. These channels exist at different widths (47, 67, 87, 107, and 127 μm) with the same depth of 20 μm. To provide a fixture and connection of the main channels of microchip to tubing, a chipholder (Micronit Microfluidics) is used which is shown in the figure 5.2.

Figure 5.1. EOR Microchips used for the micromodel test (Micronit Microfluidics)
5.2.2 Experimental Set-up

The schematic set-up used for experiments is shown in the figure 5.3. The micromodel is horizontally placed on adjustable jack stages. A precise syringe pump (Kats Scientific, NE-1010, Kats Enterprises, Denton, TX, USA) controlling a high-pressure steel syringe (KD Scientific, 2.5 mL) is used to drain and inject water into the micromodel. The stainless-steel syringe is connected to one side of micromodel with a transparent tubing. The high-pressure transparent tubing is used to observe the interface between CO\textsubscript{2} and water. On the other side, the micromodel is connected to a precise-high-pressure ISCO pump (500 HP, Teledyne ISCO, NE, USA) by another transparent tubing. A digital camera records a video during fluid injection into the micromodel. Pressure and temperature data are collected by an OMEGA PX309-3kGV pressure transducer (having 20 MPa capacity and accuracy of 0.25\%) and a T-type (Copper/Constantan, OMEGA, Norwalk, CT, USA) thermocouple (OMEGA, Norwalk, CT, USA), respectively. The sensor information is recorded using a data logger.
5.2.3 Experimental Procedure

Before starting tests, the micromodel is cleaned by injecting 5 mL absolute ethanol (Mallinckrodt Baker, ACS reagent grade,) and then 30 mL deionized water. The micromodel is dried in an oven at 120 °C for 48 h. The cleaned micromodel is assembled in the system (Fig. 5.3). CO₂ is used to flush the whole system to remove air in the micromodel, tubing, and syringe. The syringe is filled with deionized water and connected to the micromodel. Using the syringe pump, the micromodel is saturated with deionized water (DI). The ISCO pump is then used to pressurize the system to target pressures (1 or 8 MPa) gradually. The water–CO₂ interface is placed in the tubing at the ISCO pump side. The system is left under constant pressure for 24 h to reach thermodynamic equilibrium.

Water is withdrawn with a syringe pump at a constant flow rate of 0.1 μL/min while the pressure remains constant by the ISCO pump. Water flow-out continued until CO₂ percolates into the micromodel. After CO₂ percolation, water withdrawal continues for ~100 pore volumes. The amount of CO₂ in the micromodel represents the drainage CO₂ saturation. Water is then injected
into the micromodel with a constant flow rate of 0.1 μL/min which simulates the imbibition process. Water passes through the micromodel and then reaches the tubing at the ISCO pump side. The amount of remaining CO$_2$ in the micromodel represented trapped CO$_2$ saturation. An inverted microscope is used to obtain both photo and video from these micromodel channels during the test. Table 5.1 shows the different test conditions conducted in this study.

<table>
<thead>
<tr>
<th>Test</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>Water Withdrawal Flow Rate (μL/min) During Drainage</th>
<th>Water Injection Flow Rate (μL/min) During Imbibition</th>
<th>CA Measurement Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>1</td>
<td>21</td>
<td>0.1</td>
<td>0.1</td>
<td>Static &amp; dynamic</td>
</tr>
<tr>
<td>Type 2</td>
<td>8</td>
<td>21</td>
<td>0.1</td>
<td>0.1</td>
<td>Static &amp; dynamic</td>
</tr>
</tbody>
</table>

### 5.2.4 Contact Angle Measurement

Static contact angles (SCAs) are measured from photos or videos when the interface has no motion. Dynamic contact angles are measured using paused video when the interface is moving. Receding contact angles (RCA) and advancing contact angles (ACA) are observed when CO$_2$ displaces water and when water displaces CO$_2$, respectively. The contact angle measured from the prepared pictures using AutoCAD software. The contact angle measurement accuracy by AutoCAD was verified by comparing values with results from an image processing software (ImageJ with a plugin function (Contact Angle)). The accuracy and repeatability of contact angle measurement with ImageJ have been verified in [Williams et al., 2010] and [Lamour et al., 2010].

### 5.3 Results and Discussion

Figure 5.4 shows how the RCA and ACA in the micromodel are measured in same channel. When CO$_2$ displaces water in the micromodel, receding contact angles are observed (Fig. 5.4a). When water displaces CO$_2$, advancing contact angles are measured (Fig. 5.4b). Images are
captured while the interface had motion. Pore throat size is 127 μm in the figure 5.4a. Results show that the advancing contact angle is considerably higher than the receding contact angle in the same pore throat, consistent with previous studies [Dettre and Rulon E. Johnson, 1966; Chiquet et al., 2007b; Broseta et al., 2012; Saraji et al., 2013b; Arif et al., 2016a]. The difference between ACA and RCA is attributed to the blemishes on non-ideal surfaces which results in pinning the interfaces to the solid surface [Tadmor, 2004]. Various RCAs and ACAs at throat size of 47 μm in the micromodel are also shown in the figure 5.4c,d, respectively.

![Figure 5.4. Contact angle measurement in the micromodel at pressure of eight megapascals. (a) Receding contact angle at pore throat size of 127 μm; (b) Advancing contact angle at pore throat size of 127 μm; (c) Receding contact angles at pore throat size of 47 μm; (d) Advancing contact angles at pore throat size of 47 μm.](image)

5.3.1 Dynamic Contact Angle

Pinning effect of a triple line: figure 5.5 shows receding and advancing contact angles changing with various pore throat sizes (ranged from 47 μm to 127 μm) at pressure of eight megapascals for
two different tests. Results show that for the repeated tests, receding contact angles are more reproducible compared with advancing contact angles (Fig. 5.5). For example, when the pore throat size is 87 μm, standard deviations of RCA and ACA are ±4° and ±16°, respectively. This could be due to the pinning effect of a triple line during the imbibition process. Triple line, which is also called three-phase line, is the line that the three phases of the liquid, gaseous, and solid surface are intersected. During movement of the triple line on the solid surface, triple line has the chance to contacts with some spots with higher surface energy and sticks to them. This stoppage of the triple line is called pinning effect which affects the interface shape [Jafari and Jung, 2016].

Faster movement of triple lines observed during the drainage process decreases the chance of pinned triple line compared with slower movement of triple line observed during imbibition, causing similar receding contact angles during repeated tests. However, slower movement of triple line observed during the imbibition process causes stick-slip behavior of the interface and wider range of the contact angle. Khishvand et al. [Khishvand et al., 2016] have also reported a wide range of contact angles during the imbibition process using micro-CT tomography and indicated that roughness and different minerals on the surface are the main reasons for such wide variations in contact angles.

Pore throat size: receding contact angles increase with decreasing pore throat size (Fig. 5.5a), in agreement with previous studies [Li et al., 2014; Tudek et al., 2016]. Li et al. [Li et al., 2014] have reported that the contact angle increases when smaller capillary tubes are used. Using X-ray CT images, Tudek et al. [Tudek et al., 2016] have observed that CO₂ bubbles trapped in smaller pores of a sandstone have higher contact angles due to local higher pressure of CO₂ in small pores. Results of pore-network numerical models have also shown higher advancing contact angle with smaller pore size for a flooded carbonated rock sample [Juri et al., 2016].
Figure 5.5. Dynamic contact angles during drainage and imbibition processes. (a) Receding contact angle, (b) Advancing contact angle.

Receding contact angle (RCA) and advancing contact angle (ACA): Figure 5.6 shows the average and standard deviation of RCA and ACA varying with throat size. In this work, both dynamic contact angles are observed during both drainage and imbibition processes based on the interface direction. For example, when a trapped CO$_2$ bubble moves from the right side to the left side in the pore throat, right and left sides of CO$_2$ bubbles could be at advancing and receding contact angle, respectively (Fig. 5.4). Our results show that RCA is highly reproducible regardless of pore throat size (Fig. 5.6a). However, ACA shows high discrepancies (Fig. 5.6b). This could be explained by the pinning effect of a triple line [Jafari and Jung, 2016]. These results imply that the status of interface direction is more critical for defining RCA and ACA and it is not true that every contact angle in drainage and imbibition phase are RCA and ACA, respectively.

Moreover, while RCA is almost independent of injection pattern (Fig. 5.6a), ACA shows higher values during the imbibition process than that those measured during the drainage process (Fig. 5.6b). As mentioned earlier, the observed slow movement of triple line during the imbibition process results in the pinning effect which causes the increase in advancing contact angle.
Figure 5.6. Dynamic contact angles during drainage and imbibition processes. (a) Receding contact angle, (b) Advancing contact angle.

5.3.2 Static Contact Angle

Static and equilibrium contact angles: thermodynamically, the equilibrium contact angle (ECA) can only be measured at a global minimum free energy configuration, while the static contact angle (SCA) can be measured at any kinetically stable condition between advancing and receding configuration, which can be considered as a meta-stable equilibrium configuration [Ruiz-Cabello et al., 2014]. In our micromodel, interface movement is stopped in two situations. First, before percolation of the fluids (CO₂ or water) into the micromodel (percolation occurs when the front of injected fluids reaches to the other side of the micromodel), some interfaces stop at smaller pore throats due to higher capillary pressure. Second, after percolation, because almost all the injected fluid passes through the percolation path, other interfaces remain motionless. In any of these situations, static contact angles (SCA) could be measured with the motionless interfaces. However, the system of the micromodel is under fluid (water or CO₂) injection continuously. Thus, the motionless interfaces are not allowed to rest and completely approach ECA. This is the reason for low reproducibility of SCA presented in the figure 5.7. Because of different level of relaxation of the interfaces, various mode of interfaces before stoppage (i.e., receding or advancing), and
pinning effect originated from solid surface imperfection, SCA shows wide range of values for the two different tests and also for each test in any throat sizes. The range of SCA at each pore throat size is higher than that of equilibrium contact angle (ECA) measured with CO₂ or water droplet on flat surface (i.e., 8° to 45° on silica or glass surface) [Chiquet et al., 2007b; Espinoza and Santamarina, 2010; Broseta et al., 2012; Jung and Wan, 2012; Saraji et al., 2013b; Wang et al., 2013b].

![Graph](image)

Figure 5.7. Static contact angle for two repeated tests at pressure of eight megapascals.

Static contact angle during drainage and imbibition processes: figure 5.8 shows the effect of injection condition (i.e., drainage and imbibition) on average and standard deviation of static contact angle (SCA) measured at pressure of one or eight megapascals. The motionless interfaces before stoppage can be in any dynamic mode of advancing or receding. After stoppage, the shape of motionless interface is close to its dynamic mode before stoppage. Since the majority of interfaces are in receding mode during drainage, most of SCA measured in drainage behave similar to RCA. The results show SCA measured during drainage is increased with reducing pore throat size, similar to the trend observed for RCA. However, because a minority of the interfaces are in advancing mode before stoppage, the trend is not as clear as the RCA trend and reproducibility is lower.
In the same way, because majority of interfaces are in advancing mode during imbibition, the value of SCA measured during imbibition is close to ACA. As shown in the figure 5.8, there are no distinguishable relations between SCA measured during imbibition process and pore throat size, consistent with ACA results of the present study. Moreover, SCA measured during imbibition are higher than those measured during drainage process at pressure of one or eight megapascals. Khishvand et al. [Khishvand et al., 2016] have also observed that contact angle is increased when injection phase is switched from drainage to imbibition.

According to the figure 5.8, when pore throat size is small (i.e., less than 90 μm), the values of SCA during drainage and those measured during imbibition become close to each other. When CO₂ injection stops, water tends to move back into smaller pore throats due to wetting characteristic [Krevor et al., 2015a], causing smaller pore throats to mostly become under the advancing condition. Therefore, SCAs measured during both imbibition and drainage processes are similar to each other when pore throat sizes are small.

Figure 5.8. Average and standard deviation of static contact angle during drainage & imbibition processes. (a) At pressure of one megapascal, (b) At pressure of eight megapascals.
5.4 Analysis

5.4.1 Comparing Different Types of Contact Angle

Figure 5.9 shows the average and standard deviation of all contact angles (RCA, ACA, and SCA) measured in this study. These results show that SCA, RCA, and ACA have high discrepancies at each pore throat size, consistent with previous studies [Andrew et al., 2014b; Klise et al., 2016; Tudek et al., 2016]. Contact angles measured using micro-CT with rock cores and beads packs also have a wide range of values due to hysteresis of contact angle, exposure time, complex geometry, and physical and chemical heterogeneity of the surface [Andrew et al., 2014b; Klise et al., 2016; Tudek et al., 2016].

It is important to choose a proper value among various types of contact angles in order to estimate the wettability behavior of rock formation and sealing caprock. RCA is the lower boundary of contact angle. It can be used to determine injectability and capillary pressure for CO$_2$ injection into CO$_2$ storage. RCA should also be considered to determine CO$_2$ resistivity of the caprock (or capillary breakthrough pressure at the caprock) using Young–Laplace equation (Eqns. (5-3) or (5-4)).

Limitations in measuring dynamic contact angle, especially in situ measurement at pore-scale, have forced researchers to focus on SCA. However, static contact angle is of minor importance in comparison with dynamic contact angle for geological sequestration. SCA is suitable for stable conditions when there is no motion in the interface of fluids. The danger of leakage increases when CO$_2$ starts to move. Moreover, flow regime and sweep efficiency, which determine the capacity of storage, depend on dynamic parameters, including capillary number and viscosity (or mobility) ratio [Lenormand et al., 1988]. Dynamic contact angle has an important role in capillary number value.
5.4.2 Pressure Effect on Contact Angle

Jung and Wan (2012) have reported that equilibrium contact angle increases with the depth of storage. This could result in possible CO\textsubscript{2} leakage. However, RCA is more critical for evaluation of CO\textsubscript{2} resistivity of the caprock as mentioned in Section 4.1. Figure 5.10 shows that RCA at one megapascal is similar to that at eight megapascals where CO\textsubscript{2} exists as gas or liquid. This implies that the effect of wettability with increased depth of CO\textsubscript{2} storage on the risk of CO\textsubscript{2} leakage can be disregarded. However, pore sizes reduce with the increase of depth and effective stress resulting in rise of the breakthrough capillary pressure based on Young–Laplace’s equation (Eqn. (5-3) or Eqn. (5-4)). It is noteworthy that the effect of temperature is not considered here. For a comprehensive study, temperature effect and changing the CO\textsubscript{2} state into supercritical condition should be taken into account.
5.4.3 Contact Angle Hysteresis

Potential mobility of CO$_2$ bubble: figure 5.11 shows a disconnected bubble of CO$_2$ trapped by water inside a pore throat. When the pressure at the right side (P$_{\text{water1}}$) increases gradually and becomes higher than a threshold value, the CO$_2$ starts to move toward the left side. At this point, both ACA and RAC could be measured on right and left sides of a CO$_2$ bubble.

![Diagram showing a disconnected bubble of CO$_2$ trapped by water](image)

Figure 5.11. A disconnected bubble of CO$_2$ trapped by brine capillary or residual trapping.

The capillary pressure in the right and left interface can be defined as below (Eqns. (5-1) and (5-2), respectively).
\[ P_{\text{capillary}}_1 = P_{\text{CO}_2} - P_{\text{water}}_1 \quad (5-1) \]

\[ P_{\text{capillary}}_2 = P_{\text{CO}_2} - P_{\text{water}}_2 \quad (5-2) \]

where \( P_{\text{capillary}}_1 \) is the capillary pressure in the right water–CO\(_2\) interface, \( P_{\text{capillary}}_2 \) is the capillary pressure in the left water–CO\(_2\) interface, \( P_{\text{CO}_2} \) is the pressure inside the CO\(_2\) bubble, \( P_{\text{water}}_1 \) is the water pressure in the right side (where water advances), and \( P_{\text{water}}_2 \) is the pressure in the left inside (where water recedes).

By subtracting the equation (5-2) from the equation (5-1), equation (5-3) is resulted.

\[ P_{\text{water}}_1 - P_{\text{water}}_2 = P_{\text{capillary}}_2 - P_{\text{capillary}}_1 \quad (5-3) \]

From Young–Laplace’s equation:

\[ P_{\text{capillary}}_1 = \frac{2\gamma \cos(\text{ACA})}{r} \quad (5-4) \]

\[ P_{\text{capillary}}_2 = \frac{2\gamma \cos(\text{RCA})}{r} \quad (5-5) \]

By subtracting equations (5-4) and (5-5) from equation (5-3):

\[ P_{\text{water}}_1 - P_{\text{water}}_2 = \frac{2\gamma}{r} [\cos(\text{RCA}) - \cos(\text{ACA})] \quad (5-6) \]

According to equation (5-6), by an increase of the dynamic contact angle hysteresis (defined as the difference between RCA and ACA), higher water pressure difference is required before CO\(_2\) migration. In other words, mobility of the CO\(_2\) decreases as the hysteresis increases.

Figure 5.12 presents contact angle hysteresis for dynamic and static contact angles. The hysteresis of the contact angle generally increases with increasing pore throat size. The hysteresis of a dynamic contact angle at eight mega Pascal is lower than that at one mega Pascal. This implies that the mobility potential of a CO\(_2\) bubble increases with increasing CO\(_2\) storage depth when the pore throat size is constant. However, as the depth of CO\(_2\) storage increases, pores throat size
decreases due to higher effective stress [Espinoza and Santamarina, 2010]. According to the equation (5-6), when deeper aquifer site is selected for CO₂ storage, higher capillary pressure is expected due to smaller pore throat size. However, the negative effect of lower hysteresis on the contact angle should be considered for the mobility of trapped CO₂ bubble.

Relative permeability. Relative permeability is defined as a dimensionless measurement of effective permeability of a phase in a multi-phase flow system. Thus, hysteresis of relative permeability can be observed during the injection of alternate fluids (water and CO₂) into porous media [Dernaika et al., 2012]. The relative permeability of non-wetting phase (CO₂) during imbibition is known to be lower than that during drainage [Cao et al., 2016]. This is due to the following two facts: (1) contact angle hysteresis (the difference between ACA and RCA) influences the relative permeability, implying that factors affecting contact angle hysteresis such as pressure, and pore throat size should be considered to select the relative permeability in numerical simulation; and (2) the presence of trapped non-wetting phase (CO₂) influences the flow path of wetting fluid (water). When trapped non-wetting phase (CO₂) occupies larger pores, it causes the injected wetting fluid (water) to change its flow paths, resulting in decreased relative permeability [Juanes et al., 2006]. Spiteri et al. [Spiteri et al., 2005] have performed numerical modelling of a Water Alternating Gas (WAG) system for CO₂ sequestration and shown favorable results for residual trapping due to relative permeability hysteresis by decreasing leakage risk through lowering the accumulation of CO₂ plum under caprock.
5.4.4 Comparing Contact Angle of Bubbles on Flat Surface with Contact Angle of the Interfaces Covering Pore Throat inside Pores

In the literature, mostly contact angles have been measured with a CO$_2$ (or water) droplet on a flat surface. In the same way and with the similar fluid system configuration, static contact angle on a flat surface inside the micromodel can be measured (Fig. 5.13).
Contact angle of bubbles on the flat surface inside micromodel: figure 5.14 shows all type of contact angles measured in this study with the interface covering throat as well as contact angle of small bubbles on the flat surface inside micromodels. Our results reveal that a contact angle on the flat surface is not directly affected by pore throat size. However, in the figure 5.14, the contact angles of the bubbles are shown with red dots (this is shown against throat size only to show the location of measurement).

![Graph](image1)

Figure 5.14. Range of contact angle values according to various pore throat sizes. (a) At pressure of one megapascal; (b) At pressure of eight megapascals.

Average contact angles on flat surface inside micromodel at pressure of one and eight megapascals are \(62^\circ \pm 7^\circ\) and \(49^\circ \pm 21^\circ\), respectively, in agreement with Kim et al. [Kim et al., 2012] observations showing a wide range of contact angles from \(40^\circ\) to \(80^\circ\) inside a uniform micromodel. Contact angles on a flat surface in this study are higher than those shown in previous sessile drop or captive bubble tests with large droplet of water or bubble of CO\(_2\) (i.e., \(8^\circ\) to \(45^\circ\) on silica or glass surface) [Chiquet et al., 2007b; Espinoza and Santamarina, 2010; Broseta et al., 2012; Jung and Wan, 2012; Saraji et al., 2013b; Wang et al., 2013b]. This could be due to the micro-scaled CO\(_2\) bubble size on a flat surface inside the micromodel of the present study in comparison with the other studies with larger dimension of bubble ranging from a few to tens of millimeter. Shojai Kaveh et al. [Kaveh et al., 2014] have reported that smaller bubbles have higher contact angles in comparison with larger ones as a result of buoyancy force. Previous studies have
also shown that contact angles on a flat surface of rocks are smaller than those measured inside rock pores using X-ray tomography method due to gravity and buoyancy [Klise et al., 2016; Tudek et al., 2016]. These results indicate the important conclusion that glass (or rock) in pore-scale are as water-wet as already recognized by conventional macro-scale measurement.

Capillary or residual trapping: in capillary or residual trapping, CO$_2$ bubbles are entrapped inside rock pores by three mechanisms: (1) snap-off, (2) dead-end, and (3) by-passing. In snap-off, when water is invaded into a water-wet media, the water in the corner of a throat will swell gradually until it disconnects the non-wetting phase in the throat and forcibly pushes non-wetting into pore bodies [SAEEDI et al., 2012; Singh et al., 2017]. The snap-off trapping mechanism is dominant for water-wet rocks with a high aspect ratio of pore-body diameter to pore-throat diameter [Mackiewicz, 1994]. The snap-off mechanism starts when the non-wetting phase (CO$_2$) fills the pore throat first. The water layer in the corner then swells by water injection until it completely separates the non-wetting phase (CO$_2$) from the rock surface, similar to a bubble resting on a flat surface inside the micromodel as shown in the figure 5.13. In the dead-end, the non-wetting phase (CO$_2$) is trapped in dead-end pores that it carries no flow. By-passing can be defined by a pore-doublet model. When two tubes with different sizes are branched and rejoined, non-wetting fluid is trapped in the larger tube. Thus, wetting phase by-passes the larger tube and passes through the smaller tube. For both dead-end and by-passing trapping mechanisms, the water-CO$_2$ interface covers whole the pore throat. Thus, contact angles measured inside the micromodel can give more realistic values for numerical simulations compared with a contact angle of a bubble/droplet measured on a flat surface.
5.5 Conclusion

Capacity and safety prediction of geological CO₂ sequestration require a realistic wettability behavior to model multiphase immiscible fluid flow. In this chapter, a new method of pore-scale contact angle measurement was presented. A series of dynamic and static contact angles were determined inside a high-pressure glass micromodel with randomly patterned channels. In addition, contact angles of CO₂ bubbles on flat surfaces of micromodel channel were measured for comparison. Results observed in this study are summarized below:

1) Although contact angles are measured inside a highly smooth and chemically homogenous glass micromodel, a wide range of pore-scale contact angles are observed in our results, implying the complexity of the pore-scale contact angle. Thus, higher discrepancy in the contact angle is plausibly expected in real rocks containing various minerals with high roughness, irregular shape pores, and various pore throat sizes.

2) Receding contact angle (RCA) shows more reproducibility than advancing contact angle (ACA) or static contact angle (SCA). This higher reproducibility is observed for each throat size and in repeated tests. The lower reproducibility for ACA and SCA could be due to the pinning effect of the triple line.

3) Both RCA and ACA can occur during both drainage and imbibition processes. RCA shows more reproducibility even during different patterns of injections (i.e., drainage and imbibition).

4) By decreasing pore size from 127 μm to 47 μm, RCA increases from 11° to 26° at pressure of eight megapascals and from 9° to 30° at pressure of one megapascal. Local constrictions increase the pressure inside CO₂ bubbles in the small pores resulting in an increase of the interfaces curvature.
5) Generally, SCA during imbibition is higher than SCA during drainage. SCA is close to the dynamic contact angle (receding or advancing) before interface stops.

6) Although SCA is not as reproducible as RCA, it shows an increasing trend with decreasing pore throat sizes from 25° to 48° at pressure of eight megapascals and from 52° to 62° at pressure of one megapascal pressure during drainage.

7) RCA and ACA are lower boundaries of contact angles while SCA rests between them. The upper boundary is not as distinct as the lower one due to the pinning effect.

8) Hysteresis of dynamic contact angle (ACA—RCA) is higher at pressure of one megapascal than that at pressure of eight megapascals. A CO₂ bubble has higher mobility in larger depths due to lower hysteresis which is unfavorable. However, higher density of CO₂ requires its injection in deep depths (800~2000 m).

9) Contact angle of CO₂ bubbles resting on the flat surface of the micromodel channel show a wide range from 40° to 80°. Its average values at pressure of one and eight megapascals are 62° and 49°, respectively. These contact angles are much higher than those observed with sessile drop or captive bubble test on a flat plate of glass in the literature. Our results are not affected by gravity or buoyancy due to the micro-scale dimensions of the CO₂ bubble.

Our measurement method can also be applied in pore-scale models for a wide range of problems involving multiphase fluid flow in porous media, such as enhanced oil/gas recovery and methane extraction from methane-hydrate-bearing sediments.

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Chapter 6. Salinity Effect on Micro-scale Contact Angle Measured inside of a 2D Micromodel for Geological Carbon Dioxide Sequestration

6.1 Introduction

From industrial revolution, large amount of CO\textsubscript{2} has been increasingly emitted in atmosphere as a result of human activities. Parallel to developing zero-emission approaches for non-fossil fuel energies such as wind, solar, hydropower, tidal, wave, geothermal, and biomass [Inger et al., 2009; Ellabban et al., 2014; Ansari and Hughes, 2016; Rezaee and Aly, 2016], the methods of mitigating CO\textsubscript{2} emission have been developing in recent years. Geological CO\textsubscript{2} sequestration, as an efficient and economic method, has been recently developed for storing large amounts of CO\textsubscript{2} underground for long time. Depleted oil and gas reservoirs, deep saline aquifers, unminable coal seams, and methane hydrate bearing sediments are considered as the options for subsurface storage sites [Bachu and Adams, 2003; Li et al., 2006; Massarotto et al., 2010; Jafari et al., 2016; Dai et al., 2017; Zhang et al., 2018]. Deep saline aquifers are of interest because of having the highest capacity among other alternatives [IPCC, 2005]. Moreover, except geothermal energy extraction or methane recovery in very especial cases [Koide et al., 1993; Ansari et al., 2014, 2017], theses deep saline aquifers are useless comparing other storage sites and in the near future, other applications are not expected.

For a storage site, a permeable formation layer with high porosity is required for injecting and embedding large amount of CO\textsubscript{2}. Also, such a storage site needs a sealing layer of caprock on the top to stop CO\textsubscript{2} migration back to surface, leaking in atmosphere or acidifying drinkable groundwater after injection.

Structural trapping is one of the short-term mechanisms to preventing CO\textsubscript{2} leakage. The sealing caprock on the top of the storage site is expected to prevent the leakage of CO\textsubscript{2} piled up beneath the caprock. For this reason, caprock integrity has been subjected of research for detecting or
assessing the potential risk of CO$_2$ leakage through the wells and faults [Shukla et al., 2010; Mosaheb and Zeidouni, 2017a, 2017b]. Even if sealing of the wells and faults is perfectly controlled, still the leakage risk threatens the projects because the body of caprock consists of a porous medium with interconnected pores. Capillary pressure at the interface of water/CO$_2$ blocks the continuous CO$_2$ plum that is piled up under the caprock. If CO$_2$ pressure exceeds the capillary breakthrough pressure, CO$_2$ penetrates into the caprock. Therefore, the capacity and safety of the storage sites are limited by capillary force. The breakthrough capillary pressure depends on the interfacial tension of the water/brine-CO$_2$ interface, contact angle, and pore radios (pore body and pore throat size). Among the parameters influencing capillary pressure, wettability of rock, which is quantified by the contact angle, shows the highest uncertainty in literature.

Another mechanism activated in short-term is called capillary or residual trapping mechanism in which disconnected bubbles of CO$_2$ are encompassed and immobilized by water/brine inside of pores of the permeable layer formation. Higher safety makes residual trapping more favorable than the structural trapping. While large amount of connected CO$_2$ layer burdens caprock by structure trapping, the trapped bubbles of CO$_2$ are distributed all over the formation by residual trapping. Thus, an excessive pressure is not concentrated in limited points like structural trapping. Furthermore, capillary trapping accelerates the other safer long-term trapping mechanisms (i.e. solubility and mineral trapping) because a higher surface of CO$_2$ contacts with water/brine. Also, capillary pressure is governing the residual trapping mechanism.

The importance of capillary pressure and high uncertainty of wettability persuade many studies on measuring contact angle on the surfaces of rocks or minerals. Sandstone formations are common and favorable as the main rock in aquifer formations, because of relatively high porosity and water-wet behavior. To decrease the uncertainty originating from chemical heterogeneity,
roughness, and morphology of sandstone, a flat sheet of glass (quartz or silica) has been vastly used in previous studies instead of sandstone. However, a significant discrepancy has been observed in the contact angles measured on the glass surface [Chiquet et al., 2007; Sutjiadi-Sia et al., 2008; Espinoza and Santamarina, 2010; Bikkina, 2011a; Mills et al., 2011; Broseta et al., 2012; Jung and Wan, 2012; Wang et al., 2013b; Farokhpoor et al., 2013; Saraji et al., 2013; Wang et al., 2013a]. The reported contact angle ranged from 7° to 90° which clearly shows a wide range of behavior from strongly water-wet to weakly or intermediate-wet. Different thermodynamic is one of reasons in the abovementioned studies. Pressure changed from 0 to 40 MPa and temperature ranged from ~ 22°C to 123°C. Another difference can be the types of experiments including a sessile drop or a captive bubble test, type of the contact angle including static, so called equilibrium, and dynamic (i.e., advancing or receding) contact angle. Contamination on the surface and cleaning process is of importance too. Strict cleaning process resulted in lower contact angle (0° to 30° ) [Saraji et al., 2013; Iglauer et al., 2014]. Fluids condition also affects the results as the salinity of liquid phase in the above measurement changed from 0 to 7 molarity of NaCl. The degree of fluids saturation and equilibrium can be also a source of error in the measurement [Kaveh et al., 2014]. Especially, because the solubility of CO₂ in water is very sensitive to the pressure, temperature and salinity, providing perfect saturation in lab condition is difficult [Wan et al., 2014; Jafari and Jung, 2016].

Despite of the scattered data in literature, there is an important observation over the pressure dependency of contact angle on silica surface. Previous studies showed an increase of contact angle with increase of pressure when silica is subjected to supercritical CO₂ [Dickson et al., 2006; Chiquet et al., 2007; Bikkina, 2011a; Jung and Wan, 2012; Saraji et al., 2013; Tokunaga and Wan, 2013; Sarmadivaleh et al., 2015; Al-Yaseri et al., 2016]. This implies while under ambient
condition silica is strongly water-wet, the silica and rocks can be weakly water-wet under storage sites condition (i.e., high pressure and temperature). A CO$_2$-wet rock can imbibe CO$_2$ spontaneously and trapping mechanisms can be threatened, which causes leakage potential to rise. The reason of such wettability behavior remained controversial [Bikkina, 2011b, 2012; Mahadevan, 2012].

For both trapping mechanisms (i.e. structural and residual), a profound knowledge of pore-scale contact angle is needed. However, technical drawbacks forced researchers to measure contact angle indirectly or directly for a bubble/droplet with large size (i.e., several to tens of millimeter diameter). Indirect contact angle measurement only achieved a statistical sense of the parameters. For direct measurements, majority of the studies belong to a bubble of CO$_2$ or a droplet of water on a flat surface of minerals or rocks. Recent studies showed pore-scale contact angle may differ from contact angle of a bubble/droplet on a flat surface with same material [Li et al., 2014; Klise et al., 2016; Tudek et al., 2016]. Therefore, pore-scale study of contact angle is highly necessary. Recently, a number of pore-scale studies have been conducted using capillary tubes [Li et al., 2014; Qin et al., 2018], microchips [Chalbaud et al., 2009; Kim et al., 2012; Hu et al., 2017; Sharbatian et al., 2018], and rock cores [Wildenschild and Sheppard, 2013; Andrew et al., 2014; Lv et al., 2016, 2017].

Several studies have recently focused on X-ray tomography or microCT because of the unique versatility of the method in measuring contact angle inside real rocks under real thermodynamic condition [Khishvand et al., 2016; Klise et al., 2016; Iglauer and Lebedev, 2017]. MicroCT with high resolutions can capture 3D images of the wetting and non-wetting phases position and pore-shapes inside of a rock sample. Nevertheless, one of the main problems of the technique is slowness of the imaging process that makes measuring the dynamic contact angle almost
impossible. A small displacement of the water/brine-CO$_2$ interface during the measurement results in a blurry image [Khishvand et al., 2016]. Thus, even slight movement of the interface due to relaxation must be prevented [Khishvand et al., 2016; Schlüter et al., 2017]. To overcome this problem, first CO$_2$ is injected into a fully water/brine saturated sample in a drainage stage followed by an injection of water/brine back into the rock sample as an imbibition stage. Then, injection is stopped and after equilibrating the fluids for a while, static contact angles of the trapped CO$_2$ is measured. The measured static contact angle can be any values between two boundary values called receding and advancing contact angle [Dickson et al., 2006]. Dynamic contact angle, which is defined when the water/brine-CO$_2$ interface has motion, plays more important role than static contact angle because the problems like leakage depend on the mobility and motion of the non-wetting and wetting phases (CO$_2$ and water/brine respectively here).

Considering the necessity of pore-scale contact angle measurement and scarcity of such data in literature, further studies in micro-scale fluid flow for geological CO$_2$ sequestration are demanding. In the present study, a direct measurement of dynamic contact angle of saline water inside a randomly patterned 2D borosilicate micromodel is conducted. The measurement speed allows the imaging system to catch the profile of the brine-CO$_2$ interface during the flow inside the micromodel channels. The experimental set-up provides the dynamic contact angle measurement, which is not possible using other methods like x-ray tomography. The micromodel can endure high pressures and brine with different salinities can simulate the environment inside aquifers formation. In previous studies, pore-scale contact angles have been generally measured after a drainage or an imbibition tests. Therefore, there were static contact angles that could be already in receding or advancing mode before turning into static. In this study, the receding and advancing contact angle is exactly defined based on the situation of the interface and its motion.
direction. Thus, the ambiguity in the type of contact angle observed in some of the previous studies is eliminated. The micro-scale contact angles observed in the results can be used for multi-phase fluid flow and contribute to knowledge of wettability behavior of geo-materials.

6.2 Materials and Method

6.2.1 Materials and Equipment

Saline water with 0.1, 1, and 3 molarities was prepared by mixing deionized water with NaCl (Sigma-Aldrich). CO₂ with 99.99% purity was used for the experiments. High-pressure borosilicate glass microchips (Micronit Microfluidics) were used for micromodel. Microchips consists of a 1 by 2 cm random network with randomly distributed channel sizes. Two attached layers of glass with 700 μm and 1100 μm width, which only one of them etched by the randomly patterned channels, provide the micromodel morphology. While the channels have constant depth of 20 μm, the widths vary between ~ 47 to 127 μm.

6.2.2 Experimental Set-up

The Microchip is placed horizontally under an inverted microscope (Olympus), which is connected to a high-pressure steel syringe (KD Scientific, 2.5 mL) in one side. The steel syringe is mounted on a precise syringe pump (Kats Scientific) that provides a uniform fluids injection rate with high accuracy. Saline water is injected into or withdraw from the microchip by this syringe pump and steel syringe. The microchip is connected to a precise high-pressure ISCO pump (Teledyne ISCO) on the other side. This ISCO pump is filled with CO₂ and keep pressure at the target pressure, while saline water can be injected or withdrawn from the other side of the microchip. A pressure transducer (OMEGA PX309-3kGV) and thermocouples (OMEGA) monitors the pressure and temperature which are record by a data logger (Agilent 34970A Data
Acquisition). Details and schematic drawing of the used set-up are available in \[Jafari and Jung, 2017\].

### 6.2.3 Experimental Procedure

To remove organic and non-organic contaminations inside of the microchips, the microchips are cleaned by injection of 5 mL absolute ethanol following by 30 mL of deionized water. Then the microchip is dried at 120°C for 48h in an oven with constant temperature. The microchip is connected to the steel syringe and ISCO pump with transparent high pressure tubes. Whole the system is flushed by CO\(_2\) to ensure there is no air in the system. Then steel syringe is filled with saline water and saline water is injected into the microchip using the syringe pump. Then desired pressure (1 and 8 MPa) is provided by the ISCO pump. Before starting the test, the system remains 24 hours under the target pressure to ensure thermodynamic balance.

A test starts with withdrawing saline water by a continuous flow rate of 0.1 μL/min. The CO\(_2\) invades into the micromodel after a while and percolation is monitored in the channels. Around 100 pore volume of CO\(_2\) is allowed to pass through the microchip after percolation. This step is called drainage. Then the withdrawal of saline water is stopped and syringe pump is switched to inject saline water with same flow rate into the microchip in an imbibition stage. The saline water injection is continued to pass 100 pore volume of saline water through microchip. The profile of the saline water-CO\(_2\) interface in different channels is recorded by a camera through microscope.

### 6.2.4 Method of Contact Angle Measurement

As a consensus among researchers, contact angle (CA) is often measured between the fluid-fluid interface (water-CO\(_2\) here) and solid surface through the denser fluid (water here). Figure 6.1 shows the three types of contact angles measured in this chapter. Figure 6.1a and 6.1b show
dynamic contact angles, which were captured by the camera when the interface was moving. In these pictures, the channels that are appeared to have thicker black walls are occupied by the CO$_2$. The CO$_2$ water interface covers all the channel width. In other words, the three-phase contact line (or simply triple line) is sliding on the channel walls during measurement. These dynamic contact angles have two types such as receding and advancing contact angles, which are defined by the movement direction of the triple line. If CO$_2$ displaces water (or in other words if the interface is moving toward water side), the dynamic contact angle is called as a receding contact angle. Conversely, if water displaces CO$_2$, the contact angle is called as an advancing contact angle. The experiments on a flat surface can be resulted in any value between advancing and receding contact angle [Iglauer et al., 2012].

Figure 6.1c shows a bubble of CO$_2$ stick to the flat surface of a channel wall. The configuration of the fluids are similar to sessile drop or captive bubble experiment. The contact angles are measured by analyzing the interface profile using AutoCAD. The accuracy and repeatability of the measurement have been described in [Jafari and Jung, 2017]

6.3 Results and Discussion

6.3.1 Salinity Effect on Dynamic Contact Angle

Figure 6.2 shows the effect of salinity on receding contact angle (CA) at pressures of 1 and 8 MPa separately. Receding contact angles generally increase with the increase in salinity except for few channel sizes for both 1MPa and 8MPa pressures. It implies that the increase of salinity causes the wetting behavior to change from water-wet to intermediate-wet for some channel sizes.
Young’s equation presents the balance among three free energies of a droplet of a liquid on an ideal surface as following:

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL}$$  \hspace{1cm} (6-1)

where $\gamma_{SG}$, $\gamma_{SL}$, and $\gamma_{LG}$ are free energies of solid-gas, solid-liquid, and liquid-gas respectively and $\theta$ is contact angle. Contact angle can be expressed by rearranging the Young’s equation:

$$\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$  \hspace{1cm} (6-2)
The Young’s equation (Eqn. 6-2) presents that the contact angle increases with the increase of $\gamma_{SL}$ and $\gamma_{LG}$, however, contact angle decreases with the increase of $\gamma_{SG}$.

The increase of contact angle with salinity is resulted from two opposite effects as following: (1) the effect of brine-CO$_2$ interfacial energy ($\gamma_{LG}$) on increased contact angle: liquid-gas interfacial tension ($\gamma_{LG}$) increases with the increase of salinity (i.e., NaCl concentration in the electrolyte) [Bennion and Bachu, 2006; Sghaier et al., 2006; Ali et al., 2009; Chalbaud et al., 2009] resulting from the movement of cations from gas-liquid interface to bulk phase [Chalbaud et al., 2009; Leelamanie and Karube, 2013]. Leroy et al. (2010) explained “structure-making” ions escape from air/water interface into bulk water and organize the water dipoles more effectively in bulk water [Leroy et al., 2010]. Thus, the increase of $\gamma_{LG}$ results in increase of contact angle according to Young’s equation (Eqn. 6-2); (2) the effect of solid surface-liquid free energy ($\gamma_{SL}$) on decreased contact angle: Al-Zaidi and Fan, (2018) concluded that there must be some factors affecting the increase of CA other than increase of liquid-gas interfacial tension. The adsorption of ions by surface is another affecting factor which is determined by surface charge. Surface charge depends on ionic strength and pH. By increase of NaCl concentration, pH of brine increases [Al-Zaidi and Fan, 2018]. Silica surface has negative charges at moderate and high pH values (~ pH=5-10) [Subramaniam et al., 2003]. Increase of pH influences on the less presence of H\(^+\), the available negative surface charge of silica increases [Kobayashi et al., 2005]. While the increase of salt concentration results in more available Na\(^+\) in the electrolyte, the silica surface could have more negative charge due to less presence of H\(^+\) in the electrolyte, which causes the more cation of Na\(^+\), to be absorbed on the silica surface resulting in the decrease of the surface-liquid free energy ($\gamma_{SL}$) and the contract angle based on Young’s equation (Eqn. 6-2).
The increase of contact angle with salinity in this study implies that the change of brine-CO$_2$ interfacial energy ($\gamma_{LG}$) has more influence on contact angle than the solid-liquid free energy ($\gamma_{SL}$). However, the direct relations between contact angle and interfacial tension is only valid when the mineral surface is ideally homogeneous and smooth according to assumptions of Young’s equation (Eqn. 6-2). Most of mineral surfaces are not ideal, which have surface topology, chemical heterogeneity and roughness, which results in pinning effect of three phase line.

*Al-Zaidi and Fan, (2018)* showed that the contact angles on a flat glass surface increased from ~ 63° to 75° when NaCl concentration increased from 0 to 5 molarity. Their results for the contact angles inside micro-scale capillary tubes not only indicated no sensitivity to salt concentration, but also they remained much lower than contact angle on flat surface ranging from 24° to 33°. However, the abovementioned results belonged to static contact angle measurement under atmospheric pressure and the gaseous phase was air.

Figure 6.3 shows the variation of advancing contact angle at the different salinities for two 1 and 8 MPa pressures separately. Results show that no clear trend is observed between advancing contact angle and salinity. While the advancing contact angles are quite similar with different salinities at the low pressure (1 MPa pressure), advancing contact angles at 8 MPa more scatters than at 1 MPa. However, a distinct relation between salinity and advancing contact angles at both 1MPa and 8MPa pressure could not be observed.

### 6.3.2 Pressure Effect on Dynamic Contact Angle

Figure 6.4 shows the effect of pressure on receding contact angle. Receding contact angles show the higher values at higher pressure (8 MPa) in all the salinities. It implies that the glass surface inside the micromodel has a water-wet behavior at 1MPa pressure, and changes to an
intermediate-wet behavior with the increase in pressure up to 8MPa. This indicates that low pressure experiments with gaseous CO$_2$, overestimates the safety of the short-term trapping mechanisms as they show rocks are highly water-wet. Dickson et al. 2006 and Iglauer et al. 2006 also observed increase of contact angle by pressure using captive bubble test while their experiments conducted with temperature similar to our tests.

![Figure 6.3. Advancing contact angle a) at 1 MPa pressure b) at 8 MPa pressure](image)

Liu et al. (2010) concluded that contact angle on a hydrophilic surface increases with the increase of pressure and density of the CO$_2$ based on molecular dynamics [Liu et al., 2010; Iglauer et al., 2012]. The molecular dynamic computation by [Iglauer et al., 2012] showed as pressure increases to 6.7 MPa at 26° C temperature (close to our tests), an increase of contact angle to 80° is observed (Here, the condition is subcritical due to low temperature). They concluded that rapid increase in CO$_2$ density occurs at the saturation pressure for CO$_2$, which causes strong interaction between CO$_2$ and quartz surface. Siliceous materials have three types of silanols on the surface including isolated, hydrogen bonded, and inaccessible hydroxyl groups. McCool and Tripp (2005) showed not only CO$_2$ reacts with the isolated and hydrogen bonded silanols, it can react with so-called inaccessible silanols and makes them accessible under high pressure condition [McCool and Tripp, 2005].
When pressure increases from 1 to 20 MPa at 23° C temperature, free energy of water-CO$_2$ ($\gamma_{LG}$) interface drops from ~ 65 to 20 mN/m. This decrease in the denominator of the equation (6-2) can result in decrease of contact angle. However, results of Dickson et al. (2006) for a silane treated silica surface showed that the contact angle increases and the silica surface becomes more hydrophobic. Calculations showed a dramatic decrease happens in the difference of free energy of silica-water interface ($\gamma_{SG}$) and the free energy of silica-CO$_2$ interface ($\gamma_{SG}$), which is the numerator of the equation 6-2. Therefore, the resultant is decrease of $\cos \theta$ which means increase of contact angle. Capping of the silanol groups by CO$_2$ physisorption has been explained as the reason for increase of contact angle after subjection to high pressure CO$_2$ [Dickson et al., 2006].

Figure 6.5 shows the effect of pressure on advancing contact angle at different salinities. Likewise the receding contact angle, the advancing contact angle of 8 MPa shows higher values.
than those measured at 1 MPa pressure. Moreover, the increasing effect of pressure on advancing contact angle is much higher than pressure effect on receding contact angle (It can be seen by comparing the two figures of 6.4 and 6.5). While the advancing contact angle for gaseous (1MPa) shows an intermediate-wet behavior, the increase of pressure to 8 MPa causes the behavior of the glass micromodel becomes CO₂-wet in the presence of liquid CO₂.

![Figure 6.5. Advancing contact angle a) at 0.1 molarity salinity b) at 1 molarity salinity c) at 3 molarity salinity](image)

### 6.3.3 Contact Angle Hysteresis

A slug of water with any length inside a vertical capillary tube with an ideal wall surface must be easily drained out due to gravity. However, under laboratory condition, the slug is not drained if the slug length is short enough. For the mentioned capillary tube, the length of the slug determines the gravity force. Water could start to drain out when the length of slug increased
beyond a specific point. The slug resists to move downward only because the contact angle in the upper side of the slug is receding and in the lower side is advancing \cite{Joanny and de Gennes, 1984}. The difference between advancing and receding contact angle is usually referred as contact angle hysteresis \cite{Johnson and Dettre, 1964}. Therefore, it is the contact angle hysteresis that immobilizes the slug inside of the capillary tube. The contact angle hysteresis is related to roughness, chemical heterogeneity of a surface, overturning of molecular segments at the solid surface, adsorption and desorption phenomena, interdiffusion, and deformation of a surface \cite{Exstrand and Kumagai, 1997; Lam et al., 2001}. By the same reasoning, a disconnected bubble of CO$_2$ inside the rock pore is trapped between water/brine because of difference in the contact angles in the two sides. Thus, as the difference between the advancing and receding contact angle increases, the higher pressure difference or buoyancy force can be tolerated before the bubbles start to move \cite{Jafari and Jung, 2017}. Therefore, the higher hysteresis is, the more immobility is.

6.3.3.1 Salinity effect on hysteresis

Figure 6.6 represents the effect of salinity on contact angle hysteresis at 1 and 8 MPa pressures. Results show that the contact angle hysteresis decreases according to the increased salinity except few channel sizes. It implies that the risk of the disconnected CO$_2$ bubbles mobility increases with the increased salinity. Also, the density of brine increases with the salinity resulting in the increased density difference between the brine and CO$_2$, which causes the risk of gravity segregation to increase. Thus, the more amount of CO$_2$ bubbles could move upward. Note that Saraji et al. (2014) in previous study showed that contact angle hysteresis increases with the salinity from 0 to 5 M that was measured with CO$_2$ bubble on the mineral surface. It implies that contact angle hysteresis is influenced by experimental methods such as sessile drop and fluid flow inside micromodel. However, results of a study by Saraji et al. (2014) on quartz plate showed
contact angle hysteresis increases with increase of salinity from 0 to 5 M [Saraji et al., 2014].

There are several important differences between this study and results of Saraji et al. (2014). In this study, temperature is 23°C, pressure is 1 and 8 MPa, contact angle is pore-scale, and definition of the dynamic contact angle is based on the moving interface. In Saraji et al. (2014) experiments, temperature ranged from 60 to 80, pressure ranged from 13.8 to 27.6 MPa, contact angle measured by captive bubble test, and dynamic contact angle defined at the two side of the bubble on a tilting plate just at a moment before the bubble starts to move. The basic differences between the two studies and lack of overlap in the condition of two studies make comparison difficult. Further studies is necessary to deduce stronger results and analysis over the effect of salinity on contact angle hysteresis.

![Figure 6.6. Hysteresis of contact angle a) at 1 MPa pressure b) at 8 MPa pressure](image)

Water-alternating-with-gas (WAG) method is a promising technique to optimize the CO₂ storage [Ghaderi et al., 2012; Dai et al., 2014]. To accelerate the dissolution of the CO₂ into water, water with low salinity is injected alternatively between CO₂ injections in WAG technique [Vivek et al., 2017]. Injection of water with lower salinity decreases the salinity of existing water in the aquifer. Therefore, it improves the immobility of the disconnected bubbles based on our results.
6.3.3.2 Pressure effect on hysteresis

Figure 6.7 indicates effect of pressure on contact angle hysteresis for different salinities separately. For all the salinities, contact angle hysteresis increases by rising pressure from 1 MPa to 8 MPa. Saraji et al. (2014) also observed an increase of contact angle hysteresis with pressure using captive bubble test with tilting plate. Higher contact angle hysteresis in higher pressure implies that in deeper layers around 800m, which is a normal depth for geological CO$_2$ sequestration (GCS), disconnected bubble of CO$_2$ are immobilized better by surrounding water.

![Hysteresis graphs](image)

Figure 6.7. Hysteresis of contact angle a) at 0.1 molarity salinity b) at 1 molarity salinity c) at 3 molarity salinity

6.3.4 CO$_2$ Film Effect

Figure 6.8 shows the sequences of an advancing interface which is converted to a receding interface for a test with 3 molarity salinity and 8MPa pressure. In the figure 6.8a, an advancing
interface is shown in a channel with 87 micrometer width in which the interface is moving from left toward right. By advancing the interface a film of CO$_2$ on the wall of the channel remains. The trace of the film is observable in the figure 6.8b and 6.8c on the horizontal walls. Now, if the direction of the interface changes from the right to left as it is shown in the figure 6.8d, the interface is in receding condition. It is observed that when the receding interface slides on the CO$_2$ film, it has irregular shape and contact angle is higher than 90°. The interface moves with this condition until it reaches to the end of the film as it is shown in the figure 6.8e. When the interface reaches to the end of the CO$_2$ film, the concavity changes and the receding contact angle drops to a value under 90°. In another words, if interface mode changes from advancing to receding, while the interface contacts the remained CO$_2$ film, the receding CA remains higher than 90. This phenomena is observed only for the tests with 8 MPa but for any salinities. During our measurement, an extreme care is taken to distinguish the affected receding contact angle by CO$_2$ film and delete them from the reported results. However, this phenomenon implies the importance of wetting history in contact angle and fluid flow in porous medium.

Deposition of the thin film on the wall depends on the flow rate and wetting properties of the solid surface of the wall [Roman et al., 2017]. The presence of such film on the pores’ wall is very important, because it contributes to snap-off trapping of non-wetting phase. The left thin film of the wetting phase is thickened during the imbibition (when wetting phase displaces non-wetting phase) and finally surrenders and disconnects the wetting phases and traps it inside pores. An aspect ratio (pore body to pore throat size) higher than 0.5 is needed for observing snap-off mechanism [Roof, 1970], but our pore pattern does not meet this criterion.
In geological CO$_2$ sequestration where the fluids are CO$_2$ and water/brine and the solid surface is rock, it is usual to consider CO$_2$ as the non-wetting phase. However, our results of 8 MPa pressure tests showed for the advancing interface (When water displays CO$_2$), CO$_2$ is not the non-wetting phase and the glass walls behavior is CO$_2$-wet. Moreover, wetting phase can connect each other through these wetting film on the wall. This increases the available path for wetting phase to move [Hammond, 1983]. Therefore, CO$_2$ which is here the wetting phase can have the chance to escape from the new available paths.

6.3.5 Contact Angle of Bubble of CO$_2$ on Flat Surface

Static contact angle of CO$_2$ bubbles rest on the flat surface of the channels are measured (Fig. 6.1c). It is similar to conventional methods of contact angle measurement like captive bubble test,
but the difference here is the dimensions. The bubble size inside the micromodel is much smaller than the one in conventional methods by more than two orders of magnitude. The difference can effectively diminish gravity or buoyancy effect to a negligible value. The results of such contact angle measurement are presented in the figure 6.9. The channel size has no meaning here and the contact angles are shown versus the channels size only to report the measurement location.

![Figure 6.9. Contact angle of bubble on flat surface](image)

No trend has been observed between the contact angle and other parameters including pressure and salinity. However, these contact angles are much higher than the values reported for the contact angle of a CO₂ bubble/droplet on flat surface with a captive bubble or sessile drop tests in literature [Espinoza and Santamarina, 2010; Jung and Wan, 2012; Saraji et al., 2013; Iglauer et al., 2014]. Static contact angle measurement by conventional methods showed that glass is water-wet for a big range of pressure, salinity, and temperature, but micro-scale measurement shows intermediate-wet behavior. For glasses and real rocks, such difference in wetting behavior was observed by comparing the contact angle measured by sessile drop method and pore-scale x-ray tomography method [Klise et al., 2016; Tudek et al., 2016]. One reason can be removing buoyancy effect due to small size of the CO₂ bubble in our study comparing previous studies results. By eliminating
the gravity force, surface forces could dominate the wetting behavior. Therefore, imperfection in
the surface can affect the results by causing the pinning effect. Such contact angle measurement
inside micromodels also showed a wide range of values in previous study [Kim et al., 2012]. It
seems dynamic contact angle is more reliable and realistic measurement at pore scale comparing
with measuring contact angle of a bubble rest on a flat surface.

6.4 Conclusion

In order to assess the wetting behavior of saline aquifers during geological CO2 sequestration,
a series of experiment conducted by measuring dynamic and static pore-scale contact angle of
silica/brine/CO2. The measurement is conducted inside of a transparent borosilicate glass 2D
micromodel under high pressure condition with different salinities. The innovative method of
dynamic contact angle measurement yielded the following results:

1) Under both pressures of 1 and 8 MPa, by increase of salinity from 0.1M of NaCl to 3M,
receding contact angle generally increases. The average of this increase in the receding
contact angle is ~19°. However, a distinct correlation between salinity and advancing
contact angle is not observed. Moreover, a clear relation is not also observed between
dynamic contact angle and channel/pore size (ranged from ~ 47 to 137 μm) in these
experiments.

2) For every salinities, by increase of pressure from 1 MPa to 8 MPa, both receding and
advancing contact angle increases. The receding contact angle, which shows a water-wet
behavior for 1 MPa pressure, at the 8 MPa pressure indicates an intermediate-wet behavior.
The pure receding contact angle increase due to the pressure increase is ~22°. On the other
hand, the advancing contact angle, which shows an intermediate-wet behavior at 1MPa,
demonstrates a CO$_2$-wet behavior for 8 MPa pressure. The pure advancing contact angle increase due to the pressure increase was $\sim 45^\circ$.

3) Contact angle hysteresis is defined as the difference between advancing and receding contact angle. By increase of contact angle hysteresis, the inertia of a disconnected bubble of CO$_2$ against movement inside rock pores increases. The results show generally contact angle hysteresis decreases by increase pf salinity. On the other hand, by increases of pressure, higher contact angle is observed. It implies in the deeper layers, disconnected bubble of CO$_2$ have a better capillary trapping because they are immobilized better due to higher contact angle hysteresis.

4) Static contact angles of micro-scale CO$_2$ bubbles on flat surface of the micromodel channel wall showed no relation with the change of pressure and salinities. However, the results are much higher than the contact angle measured in literature with conventional methods like captive bubble and sessile drop tests. The difference can be attributed to the eliminated effect of gravity due to the smaller size of the micro-scale bubbles comparing with bubble of CO$_2$ with couple to tens of millimeter size in captive bubble test.

5) A thin film of CO$_2$ was left on the walls after CO$_2$ recedes due to water advancement. This film is of important because when the water-CO$_2$ interface is receding (CO$_2$ displaces water), the receding contact angle is higher than $90^\circ$ while the interface contacts with the thin CO$_2$ film. But after interface path the CO$_2$ films and touch the uncovered wall, receding contact angle drops to less than 90 degree.

6) Contact angle measurement of the micro-scale bubbles rest on flat surface inside the micromodel showed no trend with pressure and temperature. However, these contact angles are quite higher than the captive bubble test results in literature due to eliminating the effect
of gravity. Dynamic contact angle at pore level is more reliable and useful than static contact angle measurement for applying in numerical modelling of the fluids flow.

6.5 References:


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Chapter 7. Conclusion and Future Research

7.1 Conclusions

A series of captive bubble tests under high-pressure and high-temperature condition of geological CO₂ sequestration has been conducted to explore the wettability behavior of two minerals including silica and mica, which are abundant in sandstone and shale rocks, respectively. These measurements tried to decrease the uncertainty observed in contact angle measurement under carbon storage underground in literature. Moreover, an innovative method of measuring pore-scale contact angle at dynamic condition was introduced using a 2D microchip.

The followings are the most remarkable conclusions from the study of conventional wettability measurement method (captive bubble tests):

- During a captive bubble test under unsaturated fluids condition, it was observed that contact angle on both silica and mica substrates increased by time and by progress of dissolution of fluids into each other. This increase was less for the silica (from 35° to 42°) and higher for mica (from 25° to 68°).

- Pinning effect in triple line (contact line) was the most important factor controlling the wetting behavior of the non-ideal substrates by time. A small dissolution of the fluids could activate pinning effect in which triple line preferred to stick on the surface. During this condition, contact angle rapidly increased by time as dissolution was decreasing the other dimensions of the CO₂ bubble.

- By monitoring the change in different dimensions of the CO₂ bubble by time, a dimensionless ratio called shape factor was introduced by dividing contact line into height of the bubble. Results showed a good agreement between change of the shape factor and contact angle with time. When the shape factor was increasing, which means
a pinned stage of triple line, contact angle increased fast. Oppositely, when the shape factor remained constant, the triple was sliding on the surface and therefore, contact angle remained constant. The mica with higher heterogeneity than silica showed higher pinning effect through shape factor.

- Considering the high heterogeneity of the rock surface and unsaturated fluids under geological condition, dissolution of the CO\textsubscript{2} can be resulted in the pinning effect, increasing contact angle, decreasing capillary pressure, and increasing the risk of CO\textsubscript{2} leakage.

- Because of hardship in providing perfect thermodynamic equilibrium and fully saturated fluids during wettability measurement tests, one the sources of uncertainty and discrepancy in the literature could be unsaturated effect.

- Using two dimensionless numbers of Bond number (Bo) and shape factor, it can be concluded that heterogeneity on mica surface had more influence on the change of contact angle during CO\textsubscript{2} dissolution than decreased CO\textsubscript{2} bubble size and gravity/buoyancy effect.

- The initial contact angle after introducing CO\textsubscript{2} bubble into unsaturated water/brine and the final contact angle that could be measured before disappearing due to dissolution were compared with receding and advancing contact angles measured by other researchers on mica, respectively. The values of initial contact angles that were close to the receding contact angles increased to a value close to advancing contact angle for a heterogeneous material like mica because of dissolution and pinning effect.
The followings are the most noteworthy conclusions from the pore-scale wettability measurement study:

- Using a transparent microchip, micro-scale contact angles were measured. The imaging system was fast enough to capture the profile of the water/brine-CO$_2$ interface during moving on the walls of micromodel channels. Therefore, dynamic pore-scale contact angle can be measured which is not possible to be measured by other methods like x-ray tomography. Moreover, the type of contact angle (receding and advancing) directly defined based on the direction of the interface movement. The static contact angle measured by the x-ray tomography method can be any value between the receding and advancing contact angle depending on the situation of the interface before stopping.

- The results of micro-scale contact angle measurements showed glass (as a representative for sandstone), was not as water-wet as it is already assumed by conventional measurements in the literature. In conventional methods like sessile drop test and captive bubble test, due to the large size of the droplet/bubble, gravity and buoyancy respectively can affect the measurement, while by decreasing the size to micro level, these effects can be neglected.

- By increase of salinity from 0.1 to 3 molarity of NaCl, the receding contact angle was generally increased with an average of $\sim 19^\circ$. On the other hand, no trend between salinity and the advancing contact angle was observed.

- By increase of pressure from 1 to 8 MPa, the receding and the advancing contact angle increased $\sim 22^\circ$ and $\sim 45^\circ$, respectively. These increase changed the wetting behavior from water-wet to intermediate-wet for receding contact angle and from intermediate-wet to CO$_2$-wet for advancing contact angle.
7.2 Future Work

This dissertation was an attempt to reduce the uncertainty observed in wettability behavior of geo-materials under geological CO$_2$ sequestration condition. Lack of data and vast discrepancy observed in the available literature still encourage ongoing research studies in this area. According to the study presented in this dissertation, the following suggestions for future studies can be offered:

- In this study, micro-scale contact angle showed different behavior in comparison with contact angle measured on flat surface with larger bubble with two orders of size. Whereas the pore-scale channels, in which contact angle measured, had a limited sizes, a comprehensive effect of size can be explored by using a wider range of channel size.

- Salinity showed a significant effect on the wettability of the silica surface in this study. However, only NaCl was used to simulate salinity during the experiments. Real samples from saline aquifers shows variety of chemicals with cations with different valences. Thus, using real brine prepared from storage sites can be subject of future research.

- This study focused on the storage of carbon dioxide in saline aquifers as the storage site. For other storage sites like depleted oil and gas reservoirs, oil contamination of the surface significantly can change geo-materials wettability behavior. This research can be extended to oil and gas recovery problems.
Appendix: Permission from the Publishers

Chapter 2:

Title: Geological CO2 sequestration in saline aquifers: Implication on potential solutions of China’s power sector
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Chapter 4:

Variation of Contact Angles in Brine/CO₂/Mica System considering Short-Term Geological CO₂ Sequestration Condition

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Abstract

Geological CO₂ sequestration has been proposed as an effective solution to mitigate excessive human-emitted CO₂ in atmosphere. Knowledge of immiscible two-phase flow of CO₂-water/brine is necessary to evaluate the efficiency and safety of geological storage sites. Among forces dominating fluid flow, capillary pressure is highly important because of high uncertainty in measurement due to ambiguous wettability behavior of geopolymers. In particular, time-dependent wettability of geopolymers is of interest for predicting short-term performance of the storage site. After injection of CO₂ into an aquifer, both the CO₂ and water/brine in rocks pores are unsaturated and tend to dissolve into each other. Present study investigates the variation of contact angle on mica sheet using a captive bubble method at a wide range of pressures and salinities under unsaturated condition. Our results showed a general increase of contact angle with time. Comparison of unsaturated contact angle with previous results in the literature showed a wide span of wettability behavior, ranging from receding to advancing contact angle values reported in the literature. The observed decrease in wettability by time due to heterogeneity and pinning effect of triple line can jeopardize the safety of geological carbon sequestration projects in short-term after injection of CO₂.
Chapter 5:

**Direct Measurement of Static and Dynamic Contact Angles Using a Random Micromodel Considering Geological CO$_2$ Sequestration**

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(This article belongs to the Section Energy Sustainability)

**Abstract**

The pore-level two-phase fluids flow mechanism needs to be understood for geological CO$_2$ sequestration as a solution to mitigate anthropogenic emission of carbon dioxide. Capillary pressure at the interface of water–CO$_2$ influences CO$_2$ injectability, capacity, and safety of the storage system. Wettability usually measured by contact angle is always a major uncertainty source among important parameters affecting capillary pressure. The contact angle is mostly determined on a flat surface as a representative of the rock surface. However, a simple and precise method for determining in situ contact angle at pore-scale is needed to simulate fluids flow in porous media. Recent progresses in X-ray tomography technique has provided a robust way to measure in situ contact angle of rocks. However, slow imaging and complicated image processing make it impossible to measure dynamic contact angle. In the present paper, a series of static and dynamic contact angles as well as contact angles on flat surface were measured inside a micromodel with random pattern of channels under high pressure condition. Our results showed a wide range of pore-scale contact angles, implying complexity of the pore-scale contact angle even in a highly smooth and chemically homogenous glass micromodel. Receding contact angle (RCA) showed more reproducibility compared to advancing contact angle (ACA) and static contact angle (SCA) for repeating tests and during both drainage and imbibition. With decreasing pore size, RCA was increased. The hysteresis of the dynamic contact angle (ACA–RCA) was higher at pressure of one megapascal in comparison with that at eight megapascals. The CO$_2$ bubble had higher mobility at higher depths due to lower hysteresis which is unfavorable. CO$_2$ bubbles resting on the flat surface of the micromodel channel showed a wide range of contact angles. They were much higher than reported contact angle values observed with sessile drop or captive bubble tests on a flat plate of glass in previous reports. This implies that more precaution is required when estimating capillary pressure and leakage risk.

**Keywords:** advance contact angle; receding contact angle; static contact angle; dynamic contact angle; CO$_2$sequestration

**Figures**
Figure A.1

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Vita

Mohammad Jafari was born in Hamedan, Iran. He received his B.Sc. degree in civil engineering from Bu-Ali Sina University in 2007. Then he received his M.Sc. in geotechnical engineering from Bu-Ali Sina University in 2010. He was working as a Civil Engineer in two institutes in Hamedan before he moved to Baton Rouge Louisiana where he joined Louisiana State University to start his Ph.D. in Civil Engineering Program in spring 2014. Mohammad Jafari is currently a candidate for the degree of Doctor of Philosophy in Civil Engineering with focus in Geotechnical Engineering. During his research in Louisiana State University, Mohammad Jafari published several peer reviewed articles and conference paper.