Water Contact Angles on Quartz Surfaces under Supercritical CO₂

Sequestration Conditions: Experimental and Molecular Dynamics

Simulation Studies

Cong Chen^{a*}, Jiamin Wan^b, Weizhong Li^a and Yongchen Song^a

^a Department of Energy and Power Engineering, Dalian University of Technology, Dalian, Liaoning 116024, P. R. China

^b Earth Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

* Corresponding author. Email: congchen@dlut.edu.cn

Abstracts: The ambiguity of contact angle experimental measurements due to surface chemistry changes resulted from sample contamination and/or the degrees of reaction with supercritical CO₂ has resulted great difficulties to precisely understand the wetting behavior of CO₂ under the geological carbon sequestration (GCS) conditions. In this study, water contact angles on quartz surface under GCS conditions were investigated through the combined experimental and molecular dynamics simulation (MDS) methods. The experimental results show that water contact angles increases as ionic strength increases. The effects of pressure and temperature are very weak. The dependence of ionic strength, pressure and temperature is same for monovalent and divalent ions solutions. In the MDS, a hydroxylated quartz surface was used as the base point. A good agreement between the MDS and experimental results were obtained. Using the MDS method, a clean mineral surface with a desired surface chemistry can be constructed, which is difficult in experiments. So by comparing MDS and experimental results, the mechanisms of the reservoir wettability can be better understood. Further investigation can be made on quartz surface with different functional groups to better understand wettability alteration caused by contamination and/or CO₂ reaction.

Keywords: Contact angle, molecular dynamics simulation, supercritical CO₂, quartz, wettability, geological carbon sequestration

1. Introduction

CO₂ sequestration in deep saline aquifers has been regarded as one promising strategy to reverse the trend of increasing CO₂ emissions to the atmosphere (Altman et al., 2014). Interfacial characteristics such as interfacial tension and wettability among supercritical CO₂, brine and rock have a strong effect on capillary pressure, relative permeability and the behavior of phases (Michael et al., 2010; Song and Zhang, 2013; Tokunaga and Wan, 2013). When injecting supercritical CO₂ into saline aquifers, rock wettability among CO₂ and brine is a key factor which must be understood.

Wettability of CO₂/water/solid systems has been extensively studied by experiments (Iglauer

et al., 2015). A novel high-pressure apparatus has been developed to measure CO₂/water/solid contact angles for pressure up to 20.4 MPa (Dickson et al., 2006). They found contact angles increased significantly with CO₂ pressure for glasses with different hydrophilicities. During a comparison study between mica and quartz, a transition from strong water-wet to intermediate water-wet was captured during increasing pressures and the changing of wettability was more pronounced in the case mica (Chiquet et al., 2007). Water contact angles on glass surfaces against dense CO₂ at 313K as a function of pressure were investigated (Sutjiadi-Sia et al., 2008). It has been concluded that contact angles increased with increasing pressure in the gaseous region. However, in supercritical regime, contact angles showed little dependence on CO₂ pressure. Contact angles of the reservoir brine-reservoir rock system with dissolution of CO₂ at high pressure and elevated temperature were determined (Yang et al., 2008). According to their results, equilibrium contact angle increased as pressure increased, whereas it decreased as temperature increased. A pressurized glass micromodel was used to investigate wettability and they did not find transition from a water-wet system to an intermediate-wet system while increasing pressure up to 10 MPa (Chalbaud et al., 2009). It has been found that contact angles varied with CO₂ pressure (Espinoza and Santamarina, 2010): it increased on non-wetting surfaces such as PTEE and oil-wet quartz and slightly decreased in water-wet quartz and calcite surfaces. By repeatedly exposing samples to dense, water saturated CO₂, a permanent shift in contact angles has been found (Bikkina, 2011). However, the results were doubted and discussed in communications (Bikkina, 2012; Mahadevan, 2012). Silica wettability in CO₂-brine systems under pressure from 0.1 to 25 MPa and ionic strength from 0 to 5.0M was studied (Jung and Wan, 2012). They found that water contact angles increased as pressure increased at moderate pressures from 7-10 MPa and remained nearly constant at pressure greater than 10 MPa. Within ionic strengths they selected, water contact angles increased nearly linearly with ionic strength. Pore-scale wettability and wettability alteration in CO₂-brine-silica systems were investigated using micromodels and dewetting of silica surfaces has been found where water contact angles increased from 0° up to 80° with large increases under higher ionic strength (Kim et al., 2012). A set of contact angles for CO₂/water/rock systems were reported (Farokhpour et al., 2013). According to their data, quartz and calcite were strongly water wet and water contact angles nearly did not change with pressure, however, wettability of mica changed from strongly water-wet to intermediate water-wet as pressure increased. An increasing of water contact angles as CO₂ pressure and temperature increased were found (Saraji et al., 2013). The pressure change occurred mostly in phase transition zone and as pressure increased further, water contact angles remained unchanged. Contact angles for several solids under CO₂ sequestration conditions have been studied and the results showed that pressure and temperature affected contact angles little, however, pH value and ionic strength can give larger contact angle changing (Wang et al., 2013a). Later, they investigated CO₂ adhesion on hydrated mineral surfaces and for dynamic contact angles, adhesion increased the angle by two times (Wang et al., 2013b). Pore scale contact angle measurements at reservoir conditions were conducted using X-ray micro-tomography (Andrew et al., 2014) and they observed that CO₂-brine-carbonate system was weakly water-wet with contact angles ranging from 35° to 55°. Wettability of a CO₂/water/Bentheimer sandstone system was evaluated and the effects of saturation degree, bubble size, surface roughness and pressure were analyzed (Kaveh et al., 2014). They found that phase transition of CO₂ from subcritical to supercritical had no effect on water contact angles for Bentheimer sandstone. The effects of surfactant on wettability were investigated

and it has been found that by adding a surfactant, the contact angle in CO₂-water-SiO₂ system increased from 20°C at 0.1 MPa to 70°C at 10 MPa (Kim and Santamarina, 2014). Dynamic contact angles of CO₂/brine/quartz systems were investigated (Saraji et al., 2014). According to their results, the dynamic contact angles did not change significantly with pressure, however, they increased as brine salinity increased. Influence of temperature and pressure on quartz-water-CO₂ contact angles was investigated (Sarmadivaleh et al., 2015) and significant increase of contact angles with pressure and temperature increasing was observed. Water contact angles under N₂/CO₂ mixture atmosphere on quartz at CO₂ storage site conditions in Gippsland basin were studied (Al-Yaseri et al., 2015a). The effects of pressure, temperature, surface roughness, salt type and brine salinities on dynamic contact angles were also investigated (Al-Yaseri et al., 2015b).

The above work mentioned as well as those cited in these literature have greatly improved our understanding of wettability of CO₂-brine-mineral systems under sequestration conditions. However, the reported contact angles varied significantly for similar conditions, and were even inconsistent in their trends with respect to changes in pressure and temperature (Iglauer et al., 2015; Iglauer et al., 2014; Wan et al., 2014). The uncertainty of experimentally measured contact angle data in literature was analyzed and surface contamination was suggested as the main factor (Iglauer et al., 2014). A series of experiments with mica were conducted and several possible causes of the ambiguity problem in contact angle measurement were suggested (Wan et al., 2014): surface chemistry changing due to cleaning or initial surface roughness, contamination by adsorbing contaminants, dissolution induced by phase disequilibrium, and water film altered by CO₂-brine-mineral reactions. Among these factors, phase disequilibrium may be overcome by fully saturating brine with CO₂ before experiments and carefully controlling during experiments. A recent study showed that phase equilibrium didn't affect the contact angle within the first few minutes (Sarmadivaleh et al., 2015). The samples must be cleaned before experiments and as a result, samples may have different "history" based on different cleaning methods. Some "history" may change mineral wettability. Even a well-cleaned sample can be easily contaminated during transferring after cleaning. Surface contamination is difficult to control in experiments. A new protocol for contact angle measurement to distinguish advancing and receding contact angles was proposed (Sarmadivaleh et al., 2015). The measurement protocol may be one of the main causes of contact angle uncertainty.

Molecular dynamics simulation (MDS) is a useful tool and has been used to investigate interfacial phenomena (Hamm et al., 2013; Iglauer et al., 2012; LIU et al., 2010; McCaughan et al., 2013; Tenney and Cygan, 2014; Tsuji et al., 2013; Yan et al., 2013). By using MDS, we can construct a mineral surface with a specific surface chemistry and get an absolutely clean surface that is difficult in experiments. In fact, MDS has already been used in predicting wettability of CO₂-brine-mineral systems. The pristine silica plane with silicon atoms in the outermost layer and its partly hydroxylated modification (surface hydroxyl density 1.6/nm²) were used as a model hydrophobic surface and a model hydrophilic surface to predict wetting behavior at CO₂/water/silica interfaces (LIU et al., 2010). A fully hydroxylated silica surface was applied and contact angles between 29.9° and 52.4° when pressure ranged from 17-21 MPa were found (Bagherzadeh et al., 2012). Water contact angles on fully coordinated silica surface were predicted and contact angles about 80° under 10-15 MPa and 300K for 1M CaCl₂ solutions were found (Iglauer et al., 2012; McCaughan et al., 2013). Water/CO₂/hydrophilic silica systems at 296 K were simulated and contact angles about 20° at 13.9 MPa were got (Tsuji et al., 2013). Water

contact angles on hydrophilic and hydrophobic basal surfaces of kaolinite were predicted (Tenney and Cygan, 2014). For kaolinite gibbsite surface, contact angles predicted by CO₂ droplet method were 169°, 180° and 180° for water, 0.78M NaCl and 0.26M CaCl₂, respectively. For kaolinite siloxane surface, contact angles predicted by CO₂ droplet method were 31°, 26° and 34° and values predicted by water droplet method were 145°, 141° and 145°, respectively. For CO₂/brine/silica systems, when supercritical CO₂ is in equilibrium with brine, the pH value changes to about 3.0 (Kaszuba et al., 2003) and as a result, the formation of silanol sites is highly favorable (Hamm et al., 2013; Kim et al., 2012). Only three authors (Bagherzadeh et al., 2012; McCaughan et al., 2013; Tsuji et al., 2013) modeled silanol surfaces. However, they did not account for the effects of salinity.

In the present study, we investigated water contact angles on quartz surfaces using combined experimental and MDS methods. A divalent ion (Ca²⁺) and a monovalent ion (Na⁺) were used. The experimentally measured contact angles were compared with those predicted by MDS and the results were discussed.

2. Materials and Methods

2.1. Experimental materials and apparatus

Fig.1 Chart of contact angle measurement apparatus for CO₂/brine/rock systems under high temperature and high pressure

145 Fused quartz (Quartz Scientific Inc., purity of 99.995%, smooth, surface roughness <40nm),
146 ultra-pure DI water (resistivity $\geq 18\text{M}\Omega$, Thermo Scientific Barnstead), CO_2 (Airgas, purity
147 99.99%), NaCl (ACS grade, Aldrich) and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (ACS grade, Aldrich) were used in the
148 experiments.

149 The experiments were conducted by using a high-pressure and high-temperature contact
150 angle measurement apparatus (Fig. 1). A high P-T chamber (Temco, IFT-10) is the centerpiece.
151 Inside the chamber, a stainless steel plate was welded horizontally at the center to hold a substrate
152 by clipping onto the plate. The chamber was connected with a high P-T stirred Parr reactor (Model
153 4848) used to pre-saturate brine and CO_2 . Two injection ports are located at the top and the bottom
154 of the chamber allowing operating different fluid phases. Two syringe pumps (ISCO 500HP) were
155 used, one was connected with the high-P-T chamber to control the pressure, and another was
156 connected with the Parr reactor. Three inlets were connected with chamber for backup pressure
157 regulation, water (brine) supply and CO_2 (captive drop method, pendant drop method) droplets
158 making, respectively. A thermocouple was placed in the chamber and the chamber was covered by
159 a heating belt (Digi-Sense 8900-10). Viewing windows were opened on both sides. A high-speed
160 camera (Nikon D7000) and a light source were placed outside of viewing windows to capture
161 droplet shapes. To better control the temperature, the high P-T chamber together with the Parr
162 reactor and the connected tubing for transferring the fluids were all sit inside a thermal insulation
163 chamber.

164 2.2. Experimental methods

165 The pendant drop method was used to measure static contact angles and the captive drop
166 method was used to predict dynamic contact angles. Experiments were conducted under pressures
167 between 7-18MPa, temperatures 318-348K and ionic strength 0-9M using CaCl_2 (0-3M) and NaCl
168 (0-3M). By using captive drop method to measure dynamic contact angles, the distance between
169 needle and sample was carefully controlled in case CO_2 flux pass needle affected CO_2 /brine/quartz
170 interaction. Several tests were done to select proper distance before measurements.

171 Before contact angle measurements, it is important to prepare the mutually saturated brine
172 and CO_2 . We used the stirred Parr reactor for ≥ 12 hours under the desired P and T. Before an
173 experiment, the high P-T chamber was thoroughly cleaned using acetone and DIW. The sample
174 was cleaned with acetone and DIW before clipped onto the sample holder plate inside the chamber.
175 It should be noted that, many cleaning methods have been used in contact angle measurement
176 experiments: absolute ethanol and DIW (Kim et al., 2012), acetone and DIW (Wang et al., 2013a),
177 strongly oxidizing chemicals and oxygen plasma (Al-Yaseri et al., 2015b) and et.al. The effect of
178 cleaning protocols on contact angles is out of the scope of this study.

179 After loading the sample under the ambient conditions, the brine was injected to fill the
180 chamber. Then, the chamber was pressurized and temperature was raised to the desired values.
181 After the P and T reached to desired numbers, the liquid inside the chamber was 100% displaced
182 by the CO_2 -saturated brine from the Parr reactor under the same P-T. Then CO_2 from the Parr
183 reactor was injected to displace 10% volume of the brine in order to have both fluids co-present
184 inside the chamber. The chamber was maintained at the P-T for at least two hours before the next
185 step. CO_2 which had been fully saturated with water was slowly injected into the chamber through
186 the bottom syringe to generate bubbles. For each experimental condition, two or three quartz

plates were used and three to five CO₂ bubbles were measured for each plate. During static contact angle measurements, bubble shapes were captured for at least two hours.

2.3. MDS methods

The silica surface which has been fully hydroxylated with a silanol number density of 9.4/nm² was used as a model surface (Emami et al., 2014). The selection of model surface was discussed in the supplementary file (S0). The silica surfaces were first simulated in NPT ensemble at desired temperature and pressure before use. Equilibrium water and CO₂ structures were used to construct a box with CO₂/water interfaces. The CO₂/water box was equilibrated in NPT ensemble at desired temperature and pressure to get a system with fully saturated water and CO₂. Different numbers of water molecules saturated with CO₂ or CO₂ molecules saturated with water were selected to construct simulation cells.

Fig. 2. A snapshot of simulation cell used for simulating water droplet on quartz surface under CO₂ atmosphere in x-z plane. Quartz, ions and water molecules were illustrated in VDW format, while CO₂ molecules were drawn in CPK format.

The simulation cell contains three layers. A typical simulation cell for simulating water droplet on quartz surface under CO₂ atmosphere is illustrated in Fig. 2. The top and bottom layers are two identical quartz surfaces. The middle layer contains a water droplet in CO₂ atmosphere or a CO₂ droplet in water. A half-cylindrical droplet geometry was used instead of the traditional spherical droplet method to better predict the contact angles (Rafiee et al., 2012). Both water droplet and CO₂ droplet were simulated in this study. The simulation cell used for simulating CO₂ droplet is similar to that for water droplet. The only difference is that the middle layer is filled with a CO₂ droplet and water atmosphere.

For water droplet method, water molecules and CO₂ molecules that dissolved in water were selected from saturated water system with a half-cylindrical shape and then these molecules were placed on the bottom quartz layer. The rest of the middle layer space was filled with CO₂ molecules and water molecules that dissolved in selected from saturated CO₂ system. The procedure is similar for CO₂ droplet method. To remove interfacial stress generated by structure

construction, molecules within the droplet were fixed and the cell was simulated in NVT ensemble at desired temperature. Then, similarly, molecules outside the droplet were fixed to remove stress between quartz surface and droplet. Finally, the simulation cell was run in NVT ensemble until configuration of the droplet no longer change with time. In all simulations, quartz molecules were fixed.

In the present study, eight simulation cells were constructed and parameters for these simulation cells were summarized in Tab. 1. Force field and other simulation details can be found in the supplementary file (S1 and S2). Two quartz surfaces were used and wall effects may affect the thermodynamic behavior of fluids and perhaps the contact angle values (Gelb and Gubbins, 2000). We discussed this issue in the supplementary file (S7).

Tab. 1 Parameters of different simulation cells constructed in the present study. N_w , N_{CO_2} , N_{Na} , N_{Cl} and N_{Ca} are numbers of water molecules, CO_2 molecules, sodium cation, chlorine anion and calcium cation, respectively.

Droplet	Cell	Molarity	N_w	N_{CO_2}	N_{Na}	N_{Cl}	N_{Ca}
water	1	0	2085	4571	0	0	0
water	2	3M	2085	4571	0	226	113
water	3	3M	2085	4571	113	113	0
water	4	1M	2085	4571	0	76	38
CO_2	5	0	16594	611	0	0	0
CO_2	6	3M	16594	611	0	1792	896
CO_2	7	3M	16594	611	896	896	0
CO_2	8	1M	16594	611	0	598	299

2.4. Determination of contact angles

For experimental measurements, contact angles were calculated using an open source program ImageJ (<http://rsb.info.nih.gov/ij>). A contact angle plugin “DropSnake” (Stalder et al., 2006; Stalder et al., 2010) was applied. Several points were drawn automatically by snaking on the droplet boundary. And then these points were modified manually with the help of drop reflection. Finally, two contact angles (left and right contact points) were obtained by a piecewise polynomial fit. The determination methods of contact angles are similar to that used by other researchers (Wan et al., 2014; Wang et al., 2013a; Wang et al., 2013b).

For molecular dynamics simulations, contact angles were predicted using 2D density profiles of water. The density profiles were calculated based on a total 3ns production run. CO_2 -water contact curve was produced directly by density profiles. The quartz surface was defined as average positions for hydrogen atoms in silanol groups. Then the final 2D droplet and base surface were generated and contact angles were calculated based on tangent lines on both sides (Bagherzadeh et al., 2012). One density profile produces two contact angle data and three density profiles were generated in each simulation leading to a total of six data points for each simulation cell. The contact angles were averaged based on these data. Density profiles and tangent lines for contact angle prediction can be found in section 3.2 and the supplementary file (S5).

246 3. Results and discussions

247 3.1. Contact angles measured by experiments

248
249
250
251
252 Fig. 3 Water contact angles on quartz surface as a function of system pressure when ionic concentration is 1M,
253 temperature is 318K for monovalent and divalent ions. Right bottom: photographs of CO₂ droplet on quartz
254 surface during static contact angles measurement. A scale bar of 1mm was shown.

255
256 Water contact angles (both static and dynamic) were measured, and the results are
257 summarized in Figs. 3-5. The measured static contact angle values are between advancing and
258 receding angles as expected. For pressures from 7-18 MPa, temperatures from 318-348 K and
259 salinity from 0-3M, water contact angles are all below 30°, showing that quartz is strongly
260 hydrophilic under these conditions. In the recent literatures the experimental measured contact
261 angles from different laboratories varied up to around 90° (Iglauer et al., 2014). Recently, a higher
262 water advancing contact angle of 47° was predicted under 13 MPa and 333K (Al-Yaseri et al.,
263 2015a). They used a sessile drop method and the advancing contact angles were predicted by
264 adding water drops on the substrate to make a three phase line movement. The difference of water
265 contact angles may be caused by different measurement methods and protocols.

266 Water contact angles as a function of pressure are shown in Fig. 3. The static and dynamic

267 contact angles show no dependence on CO₂ pressure. The trends for NaCl and CaCl₂ aqueous
 268 solutions are same. In fact, the pressure dependence of water contact angles is currently under
 269 debate: (1) Contact angles increase as pressure increases in the region of phase transition (7-10
 270 MPa), and there is no or little pressure dependence in liquid and supercritical region (Dickson et
 271 al., 2006; Jung and Wan, 2012; Saraji et al., 2013; Sutjiadi-Sia et al., 2008). (2) A continuous
 272 increasing of water contact angles with pressure increasing: 0-11 MPa (Chiquet et al., 2007), 0-31
 273 MPa (Yang et al., 2008), 0-20MPa (Al-Yaseri et al., 2015b) and 0-15 MPa (Iglauer et al., 2014). (3)
 274 Water contact angles are pressure independence: 0-10 MPa (Chalbaud et al., 2009; Espinoza and
 275 Santamarina, 2010), 0-30 MPa (Farokhpour et al., 2013), 0-14 MPa (Kaveh et al., 2014) and
 276 13.8-27.6 MPa (Saraji et al., 2014). (4) Water contact angles decrease as CO₂ pressure increases in
 277 liquid phase: calcite (Espinoza and Santamarina, 2010) and quartz (Bikkina, 2011). Our measured
 278 static contact angles (experimental pressure 7-20 MPa) show slight increase in the pressure region
 279 7-10 and independent of the pressure when pressure continues to increase.

281
 282 Fig. 4 Water contact angles on quartz surface as a function of temperature when pressure is 12 MPa, ionic
 283 concentration is 1M for monovalent and divalent ions. Right bottom: photographs of CO₂ droplet on quartz surface
 284 during dynamic contact angles measurement (water advancing). A scale bar of 1.5mm was shown.

285
 286 Water contact angles as a function of temperature for 1M solutions are illustrated in Fig.4.
 287 The measured static contact angles are around 24° showing a temperature independent trend
 288 considering the experimental errors. Water receding and advancing angles follow the same trend.
 289 It seems that ion type has no effect on the temperature dependence of water contact angles. These
 290 experimental results agree well with those published in literature (Farokhpour et al., 2013; Saraji

et al., 2014). Recent studies showed that advancing water contact angles increased significantly with temperature increase (Al-Yaseri et al., 2015b; Sarmadivaleh et al., 2015). However, they applied a sessile drop method and water advancing contact angles were generated by adding several water drops (Sarmadivaleh et al., 2015) and tilting-plate technique (Al-Yaseri et al., 2015b), respectively.

296

297

298

299

300

301 Fig. 5 Water contact angles on quartz surface as a function of salinity and ionic strength when pressure is 10 MPa
 302 and temperature is 318K. Photographs of CO_2 droplet during dynamic contact angles measurement (CO_2 receding)
 303 as a function of ionic strength are also given. A scale bar of 1.5mm was shown.
 304

305 The water contact angles as a function of salinity were summarized in Fig. 5. Similar to
 306 results in literature (Broseta et al., 2012; Espinoza and Santamarina, 2010; Farokhpour et al.,
 307 2013; Jung and Wan, 2012; Kim et al., 2012; Saraji et al., 2014; Wang et al., 2013a), increasing
 308 brine salinity induces an increase in water contact angles. For NaCl aqueous solutions, water

309 contact angle increases from 21° to 25° when salinity increases from 0 to 3M. However, for CaCl₂
 310 aqueous solutions, water contact angle increases 6° within the same salinity range. For dynamic
 311 contact angles, water receding angles change slightly with salinity, but water advancing angles
 312 show a strong dependence with salinity. A recent study found a different trend where receding
 313 angles also changed significantly with salinity, but they used a tilting-plate technique to measure
 314 dynamic contact angles which is different from the technique used in the present study (Al-Yaseri
 315 et al., 2015b). For NaCl and CaCl₂ aqueous solutions, when salinity increases from 0 to 3M, water
 316 advancing angles increase 6° and 10°, respectively. The difference is due to different ionic strength
 317 for the same ions concentration showing a strong dependence of contact angle on ionic strength. A
 318 linear relationship can be found between water advancing angles and ionic strength and a linear fit
 319 leads to $\theta = 21.04 + 1.13I$ (I : °/M, $R=0.94$). For static contact angles, the slope decreases to
 320 0.84 ($R=0.91$). A similar linear relationship with a slope of 4 has been found (Jung and Wan, 2012).
 321 It should be noted that water contact angles they measured were much larger than that reported
 322 here.

323 3.2 Contact angles predicted by molecular dynamics simulations

324 3.2.1 Salinity dependence

325 Molecular dynamics simulations were performed with simulation cells 1-8. Four salinity
 326 were considered under 0M and 3M CaCl₂, 3M NaCl, and 1M CaCl₂. The temperature was fixed at
 327 318K. As the NVT ensemble was used in contact angles prediction simulation, the pressures were
 328 estimated according to final CO₂ density. CO₂ densities were calculated and averaged in bulk CO₂
 329 (water droplet method: 10 Å or more away from quartz surface and water droplet; CO₂ droplet
 330 method: central CO₂ droplet). The pressures were estimated based on NIST data book for CO₂
 331 (www.nist.gov). For cells 1-4, the calculated CO₂ densities were 587.6(5.5), 593.8(7.6), 597.1(6.3)
 332 and 583.9 (5.4) kg/m³, respectively and these data correspond to 10.8, 10.9, 10.9 and 10.8 MPa.

334

335 Fig. 6 Top: A snapshot of water droplet on quartz surface under CO₂ atmosphere after equilibration for simulation
336 cell 1 in x-z plane. Bottom left: water density profiles. Bottom right: illustration of contact angle prediction.

337

339

340 Fig. 7 Top: A snapshot of water droplet on quartz surface under CO₂ atmosphere after equilibration for
341 simulation cell 2 in x-z plane. Bottom left: CaCl₂ aqueous solution density profiles. Bottom right: illustration of
342 contact angle prediction.

344

346

348 Fig. 8 Top: A snapshot of water droplet on quartz surface under CO₂ atmosphere after equilibration for simulation
 349 cell 3 in x-z plane. Bottom left: NaCl aqueous solution density profiles. Bottom right: illustration of contact angle
 350 prediction.

351 Fully hydroxylated silica surface is hydrophilic (Duval et al., 2002; Emami et al., 2014). As
 352 expected, water droplets wet the silica surface on all conditions studied. Water droplet spreading
 353 with simulation time can be found in the supplementary file (S3). When water droplet shape
 354 stopped to change with time, density profiles were produced. Then water contact angles were
 355 calculated based on density profiles. The results for pure water droplets are illustrated in Fig. 6,
 356 indicating the predicted water contact angle is 22.6° which agrees well with experimental results
 357 in this study (20°-21°). Our result is also in accord with other molecular dynamics simulation
 358 predictions (Tsuji et al., 2013): 20° under 296K and 13.9 MPa. A similar hydroxylated silica
 359 surface was also used by other authors, but they got water contact angles nearly 30° for water
 360 (Bagherzadeh et al., 2012). It should be noted that they used different initial setup and much
 361 shorter simulation time (2ns). Several authors applied different silica surfaces and their predicted
 362 results were between 60° and 90° (Iglauer et al., 2012; LIU et al., 2010; McCaughan et al., 2013).

363 The results for water droplets of 3M CaCl₂ and 3M NaCl are presented in Figs. 7 and 8,
 364 respectively. When salinity increases to 3M, water contact angles increase to 29.5° and 35.5° for
 365 NaCl and CaCl₂ aqueous solutions, respectively. These values are reasonable compared with
 366 experimental results (20°-27° and 20°-31°). The water contact angle for 1M CaCl₂ solution has
 367 also been predicted and the results are illustrated in the supplementary file (S5). The predicted
 368 value is 28.7° and agrees well with the experimental result of 20°-26°. Much higher water contact
 369 angles (about 80°) were predicted at 300K and pressures from 10-20 MPa (McCaughan et al.,
 370 2013). But they used a half-hydroxylated quartz surface (silanol density around 4.6 OH/nm²) and a
 371 fully coordinated quartz surface. It should be noted that to the best of our knowledge, there are no
 372 MDS predictions of water contact angles on fully hydroxylated quartz for NaCl and CaCl₂

aqueous solutions, and we cannot compare our results with other MDS studies. However, the accordance of our simulation results with experimental results shows that molecular dynamics simulation is a good tool to predict contact angles as long as proper simulation protocol and force field are selected and the results are quantitatively comparable with experimental results.

Due to the hydrophilic nature of fully hydroxylated silica surface, CO₂ droplets with initial cylindrical geometry dewet from the surface. A clear dewetting with simulation time was found during MDS, however, CO₂ droplets finally detached from the surface. As a result, it's impossible to predict contact angles using CO₂ droplet method. The dewetting process of CO₂ droplet and density profiles can be found in the supplementary file (S4 and S6). The final CO₂ droplet shapes were summarized in Fig. 9. The detaching distances are different with the order of pure water > 3M NaCl (1M CaCl₂) > 3M CaCl₂. In fact, this is caused by different water contact angles. A similar phenomenon was found during simulating contact angles on basal surfaces of kaolinite using a CO₂ droplet method (Tenney and Cygan, 2014).

Fig. 9 Snapshots of CO₂ droplets on silica surface. The snapshots are in x-z plane. Quartz and water molecules are drawn in CPK format, CO₂ molecules and ions are illustrated in VDW format.

3.2.2 Pressure and temperature dependence

To study the effects of pressure and temperature, four additional simulation runs were produced. The final coordination files for simulation cell 2 (after 15ns run) were used as a start point. The number of CO₂ molecules was modified to change bulk CO₂ density according to desired pressure. Two pressures were considered: 7 MPa and 12 MPa with the constant temperature 318 K, and 10.9 MPa at 333 K.

The predicted water contact angles for different pressures are $32.2^\circ (\pm 2.8)$ and $35.8^\circ (\pm 4.3)$, respectively. The calculated water contact angle at 333K was $36.2^\circ (\pm 4.1)$. As shown in Fig. 7, water contact angles for simulation cell 2 at 10.9 MPa and 318K is $35.5^\circ (\pm 3.6)$. These data implies that water contact angles show no dependence with pressure and temperature as found by our experimental results.

3.2.3 MDS prediction of contact angles on “CO₂-reacted” quartz surface

CO₂ sorption on silica surfaces were studied by experiments (Di Giovanni et al., 2001; McCool and Tripp, 2005; Roque-Malherbe et al., 2010; Tripp and Combes, 1998) and molecular simulation studies (Vishnyakov et al., 2008). To study the effect of CO₂ pre-reaction on wettability, we conduct simulations with CO₂ -reacted quartz surface. It should be noted that, the reaction mentioned here is physic-sorption and functional groups on quartz surface are not changed.

At first, water cylindrical droplet in simulation cell 2 (initial structure, not equilibrated) was removed and replaced by CO₂ molecules to form a new simulation cell containing CO₂ and quartz. The new generated cell was simulated in NVT ensemble for 12ns to obtain an equilibrium structure containing CO₂ and pre-reacted quartz surface. Then, water cylindrical droplet was placed into the equilibrium structure by removing a certain number of CO₂ molecules. In order not to change the CO₂ -quartz structure near the quartz surface, water droplet was placed above surface with a distance of 8 Å. The new cell with water droplet was simulated and water contact angles were calculated.

417 The snapshots of water droplets as a function of simulation time were illustrated in Fig. 10.
 418 The CO₂-layer was displaced by water molecules quickly (less than 2ns). However, a small
 419 amount of CO₂ molecules were left between quartz surface and water molecules at the middle
 420 bottom of the droplet. The number of captured CO₂ molecules decreased as simulation went on.
 421 But the speed was rather slow. In the meantime, water molecules spread on quartz surface and the
 422 droplet shape became same as that in Fig. 7 after 10 ns. This implies that the CO₂ layer after CO₂
 423 -quartz pre-reaction does not change wettability. It has been proposed that physic-sorption
 424 (Dickson et al., 2006) and/or hydrogen bonds (Vishnyakov et al., 2008) between CO₂ and quartz
 425 exist. Based on our results, the physic-sorption and hydrogen bonds between CO₂ and quartz
 426 seems very weak compared with water-quartz interaction. It should be noted that we used a flat
 427 fully hydroxylated surface and the roughness was not considered.

428
 429
 430
 431
 432
 433

437 Fig. 10 Snapshots of water droplets as a function of simulation time. The water droplet was initially placed above
 438 the quartz surface at a distance of 8 Å. The snapshots are in x-z plane. For clarity, salt ions are not shown.

439 **4 Conclusions**

440 Static and dynamic contact angles of supercritical CO₂ and brine on quartz surface under CO₂
441 sequestration conditions were investigated using a high-pressure and high-temperature contact
442 angle measurement apparatus. The results show that water contact angles increases as ionic
443 strength increases. However, the effects of pressure and temperature are insignificant. The trend of
444 the dependence of ionic strength, pressure and temperature seems to be the same for monovalent
445 and divalent ions solutions. Water static contact angles were studied using molecular dynamics
446 simulation methods. The predicted water contact angles agree well with those obtained by
447 laboratory measurements. The results of molecular dynamics simulation are qualitatively
448 consistent with the experimental results, indicating that molecular dynamics simulation is a
449 suitable tool for predicting water contact angles under CO₂ sequestration conditions. Due to the
450 ambiguity during contact angle experimental measurements, molecular dynamics simulation can
451 become very useful to help improve our understanding of wettability on mineral surface for CO₂
452 /brine systems.

453 Water contact angles on a flat, CO₂ pre-reacted quartz surface have also been simulated. The
454 results show that the adsorbed CO₂ on quartz surface can be easily replaced by water droplet. The
455 final water contact angle does not change although some CO₂ molecules are captured. The results
456 on rough surface maybe different and further studies are required.

457 A fully hydroxylated quartz surface was applied during molecular dynamics simulations. The
458 accordance of experimental and simulation results shows that under these experimental conditions,
459 silanol groups are dominant on quartz surface. Under real CO₂ sequestration environment, the
460 functional groups on quartz surface are complex: Si-O-H, Si-O-Si, Si-O-ions and their
461 combination (Emami et al., 2014). It has been shown that siloxane is hydrophobic(Tenney and
462 Cygan, 2014) and wettability depends on the ratio of silanol vs. siloxane (Emami et al., 2014).
463 Further investigation should be made on quartz surface with different functional groups to better
464 understand wettability alteration caused by contamination and/or CO₂ reactions.

465 **Acknowledges**

466 This research was supported by the following projects: project 51206016 funded by National
467 Natural Science Foundation of China (NSFC), the Doctoral Startup Funds of Liaoning Province
468 (20121021) and the Fundamental Research Funds for the Central Universities (DUT14LAB13).
469 Grateful acknowledge should be sent to China Scholarship Council for the financial support for Dr.
470 Chen during staying in U.S.A. Dr. Wan's involvement in this work and the laboratory facility were
471 supported by the Center for Nanoscale Control of Geologic CO₂, an Energy Frontier Research
472 Center funded by the U.S. Department of Energy, Office of Science, and Office of Basic Energy
473 Sciences under Award Number DE-AC02-05CH11231. Thank Tetsu K. Tokunaga (Lawrence
474 Berkeley National Lab) for reading this manuscript and helpful comments. We thank Drs.
475 Yongman Kim, Shibo Wang, Prem Bikkina and Wenming Dong (Lawrence Berkeley National Lab)
476 for the kind help during experiments, and the fruitful discussion on contact angle experiments. We
477 also thank Computing Center in Department of Energy and Power Engineering of Dalian
478 University of Technology for providing parallel computing environment.

479 **References**

- 480 Al-Yaseri, A., Sarmadivaleh, M., Saeedi, A., Lebedev, M., Barifcani, A., Iglauder, S., 2015a. N-2 + CO₂
481 + NaCl brine interfacial tensions and contact angles on quartz at CO₂ storage site conditions in the
482 Gippsland basin, Victoria/Australia. *J. Pet. Sci. Eng.* 129, 58-62.
- 483 Al-Yaseri, A.Z., Lebedev, M., Barifcani, A., Iglauder, S., 2015b. Receding and advancing (CO₂ + brine
484 + quartz) contact angles as a function of pressure, temperature, surface roughness, salt type and salinity.
485 *The Journal of Chemical Thermodynamics*.
- 486 Altman, S.J., Aminzadeh, B., Balhoff, M.T., Bennett, P.C., Bryant, S.L., Cardenas, M.B., Chaudhary,
487 K., Cygan, R.T., Deng, W., Dewers, T., DiCarlo, D.A., Eichhubl, P., Hesse, M.A., Huh, C., Matteo,
488 E.N., Mehmani, Y., Tenney, C.M., Yoon, H., 2014. Chemical and Hydrodynamic Mechanisms for
489 Long-Term Geological Carbon Storage. *J. Phys. Chem. C* 118, 15103-15113.
- 490 Andrew, M., Bijeljic, B., Blunt, M.J., 2014. Pore-scale contact angle measurements at reservoir
491 conditions using X-ray microtomography. *Advances in Water Resources* 68, 24-31.
- 492 Bagherzadeh, S.A., Englezos, P., Alavi, S., Ripmeester, J.A., 2012. Influence of Hydrated Silica
493 Surfaces on Interfacial Water in the Presence of Clathrate Hydrate Forming Gases. *J. Phys. Chem. C*
494 116, 24907-24915.
- 495 Bikkina, P.K., 2011. Contact angle measurements of CO₂-water-quartz/calcite systems in the
496 perspective of carbon sequestration. *Int. J. Greenh. Gas Control* 5, 1259-1271.
- 497 Bikkina, P.K., 2012. Reply to the comments on "Contact angle measurements of
498 CO₂-water-quartz/calcite systems in the perspective of carbon sequestration". *Int. J. Greenh. Gas*
499 *Control* 7, 263-264.
- 500 Chalbaud, C., Robin, M., Lombard, J.-M., Martin, F., Egermann, P., Bertin, H., 2009. Interfacial
501 tension measurements and wettability evaluation for geological CO₂ storage. *Advances in Water*
502 *Resources* 32, 98-109.
- 503 Chiquet, P., Broseta, D., Thibeau, S., 2007. Wettability alteration of caprock minerals by carbon dioxide
504 *Geofluids* 7, 112-122.
- 505 Di Giovanni, O., Dorfler, W., Mazzotti, M., Morbidelli, M., 2001. Adsorption of supercritical carbon
506 dioxide on silica. *Langmuir* 17, 4316-4321.
- 507 Dickson, J.L., Gupta, G., Horozov, T.S., Binks, B.P., Johnston, K.P., 2006. Wetting phenomena at the
508 CO₂/water/glass interface *Langmuir* 22, 2161-2170.
- 509 Duval, Y., Mielczarski, J.A., Pokrovsky, O.S., Mielczarski, E., Ehrhardt, J.J., 2002. Evidence of the
510 existence of three types of species at the quartz-aqueous solution interface at pH 0-10: XPS surface
511 group quantification and surface complexation modeling. *Journal of Physical Chemistry B* 106,
512 2937-2945.
- 513 Emami, F.S., Puddu, V., Berry, R.J., Varshney, V., Patwardhan, S.V., Perry, C.C., Heinz, H., 2014. Force
514 Field and a Surface Model Database for Silica to Simulate Interfacial Properties in Atomic Resolution.
515 *Chem. Mat.* 26, 2647-2658.
- 516 Espinoza, D.N., Santamarina, J.C., 2010. Water-CO₂-mineral systems: Interfacial tension, contact angle,
517 and diffusion—Implications to CO₂ geological storage. *Water Resources Research* 46, W07537.
- 518 Farokhpoor, R., Bjorkvik, B.J.A., Lindeberg, E., Torsaeter, O., 2013. Wettability behaviour of CO₂ at
519 storage conditions. *Int. J. Greenh. Gas Control* 12, 18-25.
- 520 Gelb, L.D., Gubbins, K.E., 2000. Phase separation in confined systems (vol 62, pg 1573, 1999). *Rep.*
521 *Prog. Phys.* 63, 727-727.

522 Hamm, L.M., Bourg, I.C., Wallace, A.F., Rotenberg, B., 2013. Molecular Simulation of CO₂- and
523 CO₃-Brine-Mineral Systems, in: D.J. DePaolo, D.R. Cole, A. Navrotsky, I.C. Bourg (Eds.),
524 Geochemistry of Geologic CO₂ Sequestration. Mineralogical Soc Amer, Chantilly, 189-228.

525 Iglauer, S., Mathew, M.S., Bresme, F., 2012. Molecular dynamics computations of brine-CO₂
526 interfacial tensions and brine-CO₂-quartz contact angles and their effects on structural and residual
527 trapping mechanisms in carbon geo-sequestration. *Journal of Colloid and Interface Science* 386,
528 405-414.

529 Iglauer, S., Pentland, C.H., Busch, A., 2015. CO₂ wettability of seal and reservoir rocks and the
530 implications for carbon geo-sequestration. *Water Resources Research* 51, 729-774.

531 Iglauer, S., Salamah, A., Sarmadivaleh, M., Liu, K.Y., Phan, C., 2014. Contamination of silica surfaces:
532 Impact on water-CO₂-quartz and glass contact angle measurements. *Int. J. Greenh. Gas Control* 22,
533 325-328.

534 Jung, J.-W., Wan, J., 2012. Supercritical CO₂ and Ionic Strength Effects on Wettability of Silica
535 Surfaces: Equilibrium Contact Angle Measurements. *Energy & Fuels* 26, 6053-6059.

536 Kaszuba, J.P., Janecky, D.R., Snow, M.G., 2003. Carbon dioxide reaction processes in a model brine
537 aquifer at 200 degrees C and 200 bars: implications for geologic sequestration of carbon. *Appl.*
538 *Geochem.* 18, 1065-1080.

539 Kaveh, N.S., Rudolph, E.S.J., van Hemert, P., Rossen, W.R., Wolf, K.H., 2014. Wettability Evaluation
540 of a CO₂/Water/Bentheimer Sandstone System: Contact Angle, Dissolution, and Bubble Size. *Energy*
541 *& Fuels* 28, 4002-4020.

542 Kim, S., Santamarina, J.C., 2014. Engineered CO₂ injection: The use of surfactants for enhanced
543 sweep efficiency. *Int. J. Greenh. Gas Control* 20, 324-332.

544 Kim, Y., Wan, J.M., Kneafsey, T.J., Tokunaga, T.K., 2012. Dewetting of Silica Surfaces upon Reactions
545 with Supercritical CO₂ and Brine: Pore-Scale Studies in Micromodels. *Environ. Sci. Technol.* 46,
546 4228-4235.

547 LIU, S., YANG, X., QIN, Y., 2010. Molecular dynamics simulation of wetting behavior at
548 CO₂/water/solid interfaces. *Chinese Science Bulletin* 55, 2252-2257.

549 Mahadevan, J., 2012. Comments on the paper titled "Contact angle measurements of
550 CO₂-water-quartz/calcite systems in the perspective of carbon sequestration": A case of contamination?
551 *Int. J. Greenh. Gas Control* 7, 261-262.

552 McCaughan, J., Iglauer, S., Bresme, F., 2013. Molecular Dynamics Simulation of Water/CO₂-quartz
553 Interfacial Properties: Application to Subsurface Gas Injection. *Energy Procedia* 37, 5387-5402.

554 McCool, B., Tripp, C.P., 2005. Inaccessible hydroxyl groups on silica are accessible in supercritical
555 CO₂. *Journal of Physical Chemistry B* 109, 8914-8919.

556 Michael, K., Golab, A., Shulakova, V., Ennis-King, J., Allinson, G., Sharma, S., Aiken, T., 2010.
557 Geological storage of CO₂ in saline aquifers-A review of the experience from existing storage
558 operations. *Int. J. Greenh. Gas Control* 4, 659-667.

559 Rafiee, J., Mi, X., Gullapalli, H., Thomas, A.V., Yavari, F., Shi, Y.F., Ajayan, P.M., Koratkar, N.A.,
560 2012. Wetting transparency of graphene. *Nature Materials* 11, 217-222.

561 Roque-Malherbe, R., Polanco-Estrella, R., Marquez-Linares, F., 2010. Study of the Interaction between
562 Silica Surfaces and the Carbon Dioxide Molecule. *J. Phys. Chem. C* 114, 17773-17787.

563 Saraji, S., Goual, L., Piri, M., Plancher, H., 2013. Wettability of Supercritical Carbon
564 Dioxide/Water/Quartz Systems: Simultaneous Measurement of Contact Angle and Interfacial Tension
565 at Reservoir Conditions. *Langmuir* 29, 6856-6866.

566 Saraji, S., Piri, M., Goual, L., 2014. The effects of SO₂ contamination, brine salinity, pressure, and
 567 temperature on dynamic contact angles and interfacial tension of supercritical CO₂/brine/quartz
 568 systems. *Int. J. Greenh. Gas Control* 28, 147-155.
 569 Sarmadivaleh, M., Al-Yaseri, A.Z., Iglauer, S., 2015. Influence of temperature and pressure on
 570 quartz-water-CO₂ contact angle and CO₂-water interfacial tension. *Journal of Colloid and Interface*
 571 *Science* 441, 59-64.
 572 Song, J., Zhang, D.X., 2013. Comprehensive Review of Caprock-Sealing Mechanisms for Geologic
 573 Carbon Sequestration. *Environ. Sci. Technol.* 47, 9-22.
 574 Stalder, A.F., Kulik, G., Sage, D., Barbieri, L., Hoffmann, P., 2006. A snake-based approach to accurate
 575 determination of both contact points and contact angles. *Colloid Surf. A-Physicochem. Eng. Asp.* 286,
 576 92-103.
 577 Stalder, A.F., Melchior, T., Mueller, M., Sage, D., Blu, T., Unser, M., 2010. Low-bond axisymmetric
 578 drop shape analysis for surface tension and contact angle measurements of sessile drops. *Colloid Surf.*
 579 *A-Physicochem. Eng. Asp.* 364, 72-81.
 580 Sutjiadi-Sia, Y., Jaeger, P., Eggers, R., 2008. Interfacial phenomena of aqueous systems in dense carbon
 581 dioxide. *The Journal of Supercritical Fluids* 46, 272-279.
 582 Tenney, C.M., Cygan, R.T., 2014. Molecular Simulation of Carbon Dioxide, Brine, and Clay Mineral
 583 Interactions and Determination of Contact Angles. *Environ. Sci. Technol.* 48, 2035-2042.
 584 Tokunaga, T.K., Wan, J.M., 2013. Capillary Pressure and Mineral Wettability Influences on Reservoir
 585 CO₂ Capacity, in: D.J. DePaolo, D.R. Cole, A. Navrotsky, I.C. Bourg (Eds.), *Geochemistry of Geologic*
 586 *CO₂ Sequestration*. Mineralogical Soc Amer, Chantilly, 481-503.
 587 Tripp, C.P., Combes, J.R., 1998. Chemical modification of metal oxide surfaces in supercritical CO₂:
 588 The interaction of supercritical CO₂ with the adsorbed water layer and the surface hydroxyl groups of a
 589 silica surface. *Langmuir* 14, 7350-7352.
 590 Tsuji, S., Liang, Y.F., Kunieda, M., Takahashi, S., Matsuoka, T., 2013. Molecular Dynamics
 591 Simulations of the CO₂-Water-Silica Interfacial Systems. *Ghgt-11* 37, 5435-5442.
 592 Vishnyakov, A., Shen, Y.Y., Tomassone, M.S., 2008. Interactions of silica nanoparticles in supercritical
 593 carbon dioxide. *Journal of Chemical Physics* 129.
 594 Wan, J.M., Kim, Y., Tokunaga, T.K., 2014. Contact angle measurement ambiguity in supercritical
 595 CO₂-water-mineral systems: Mica as an example. *Int. J. Greenh. Gas Control* 31, 128-137.
 596 Wang, S.B., Edwards, I.M., Clarens, A.F., 2013a. Wettability Phenomena at the CO₂-Brine-Mineral
 597 Interface: Implications for Geologic Carbon Sequestration. *Environ. Sci. Technol.* 47, 234-241.
 598 Wang, S.B., Tao, Z.Y., Persily, S.M., Clarens, A.F., 2013b. CO₂ Adhesion on Hydrated Mineral
 599 Surfaces. *Environ. Sci. Technol.* 47, 11858-11865.
 600 Yan, M.Q., Yang, X.N., Lu, Y.J., 2013. Wetting behavior of water droplet on solid surfaces in solvent
 601 environment: A molecular simulation study. *Colloid Surf. A-Physicochem. Eng. Asp.* 429, 142-148.
 602 Yang, D., Gu, Y., Tontiwachwuthikul, P., 2008. Wettability determination of the reservoir
 603 brine-reservoir rock system with dissolution of CO₂ at high pressures and elevated temperatures
 604 *Energy & Fuels* 22, 504-509.
 605
 606

607 **Graphic: Water contact angles as a function of ionic**
 608 **strength.**

609

610

611

612

613

614

615

616

617

618

619

620