

Molecular Dynamics Simulation of CO₂-fluid and CO₂-mineral interfacial properties: Application to subsurface gas injection (CCS projects)

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Abstract

Global Warming due to Carbon Dioxide (CO₂) emissions from fossil fuel consumption remains an extremely difficult problem to mitigate. One of the many purposed methods to tackle rising emissions of CO₂ is subsurface injection into geological formations known as Carbon Capture and Storage (CCS).

A major challenge, that projects involving subsurface gas injection have, is predicting the amount of gas that will be trapped in the formation effectively and safely. A major contributing factor to this uncertainty is knowing the interfacial tension and contact angle between the subsurface rocks, formation water and CO₂.

The two main difficulties with employing experimental work to estimate these parameters are partially contradicting results and accurately recreating the range of subsurface conditions.

One of the ways to recreate the range of subsurface conditions and to explain contradicting results with respect to interfacial interactions is the use of Molecular Dynamics computer simulations.

In the first half of this report we have investigated how divalent salts affect the CO₂/water/quartz contact angle, and how N₂/water/quartz and H₂S/water/quartz contact angles compare to the CO₂/water quartz contact angles. The quartz used for these simulations was a fully coordinated quartz crystal taken from Iglauer et al. 2012. The results from the simulations suggested that divalent salt had negligible effect on the contact angle, and that N₂/water/quartz contact angles were significantly lower while H₂S/water/quartz contact angles were significantly higher compared to CO₂/water/quartz contact angles.

In the second half of this report we have developed a hydroxylated quartz crystal model and simulated the water contact angle on this surface. The contact angle was observed to be significantly reduced compared to angles on the fully coordinated quartz surface.

Introduction

Rising levels of anthropogenic Carbon Dioxide (CO₂) since the industrial revolution has been widely considered as a principal cause of rising global temperatures (Mann et al. 2003). Carbon Capture and Storage (CCS) has been proposed and reviewed as a possible way to mitigate these CO₂ emissions from fossil fuel consumption. The International Energy Agency (EIA 2009) predicts that CCS could account for up to a 19% reduction of global CO₂ emissions. Currently in CCS projects CO₂ has been taken from gas processing and injected into the subsurface for Enhanced Oil Recovery in depleting oil fields such as Shute Creek, USA. Alternatively it has been injected into a nearby saline aquifer for disposal such as in the Sleipner field, Offshore Norway (Håvard et al. 2008). Hydrogen sulfide (H₂S) is another gas with negative environmental impact commonly referred to as acid gas. It has also been injected into the subsurface for disposal by many operators (Chakma 1997). This is due to the normal process of disposal, the Claus process, becoming less economical in recent times (Jamaluddin et al. 1996).

For the injected gas to remain present in the subsurface it must be trapped sufficiently, i.e. to an extent where the relative permeability of the gas must be approximately zero. There are generally considered four main mechanisms present that trap CO₂ in subsurface formation:

1. Structural trapping, where a layer of rock (commonly referred to as the caprock) is present with a seal, which has negligible permeability. This then prevents the buoyant gas from flowing upwards (Hesse et al. 2008).
2. Residual trapping, also known also as capillary trapping where the gas is trapped as bubbles by capillary forces present in the pore space of the rock (Qi et al. 2009, Iglauer et al. 2011b).
3. Dissolution trapping; where the injected CO₂ dissolves into formation brine. The brine now saturated with CO₂ sinks due to an increase in density (Riaz et al. 2006);
4. Mineral trapping; where the CO₂ is trapped by reacting with host rock and minerals in the formation brine to form solid materials (Xu et al. 2003). Note that this trapping mechanism (mineral) is considered to take place over a longer time frame in comparison with the other trapping mechanisms (structural, residual and dissolution).

The focus of this work is on predicting the extent of *Structural and Residual Trapping*; specifically how both these mechanisms depend on capillary forces.

Capillary forces are physically expressed as capillary pressure, which is defined as the difference in pressure between the non-wetting and wetting phase (Akins 2009). The Young-Laplace equation states the following;

$$\Delta P = P_c = \frac{2\gamma \cos \theta}{r} \dots \dots \dots (1)$$

P_c (capillary pressure) is proportional to the interfacial tension (γ) between the two fluids and the cosine of the contact angle that the interface makes with the substrate while inversely proportional to the effective radius of the pore (r), assuming the pore has a circular cross-section. Considering the force balance between buoyancy forces-capillary forces:

$$h = \frac{P_c}{\Delta \rho g} \dots \dots \dots (2)$$

$\Delta \rho$ (difference in density between the two phases), g (gravitational acceleration) and h (column height), the amount of buoyant gas trapped safely by structural trapping. Combining equations (1) and (2):

$$h = \frac{\gamma \cos \theta}{r \Delta \rho g} \dots \dots \dots (3)$$

See Naylor et al (2011) for a more detailed outline of the derivation and discussion on CO₂ column heights stored below caprocks.

With respect to structural trapping, h determines the volume of gas stored beneath the caprock, $\Delta \rho$ and θ will be the density difference and contact angle respectively between gas and the brine and P_c is the capillary entry pressure of the caprock. If the pressure is above this capillary entry pressure stored gas can break through the caprock. Though methods are being developed to monitor (Sweatwan et al. 2010) and remediate (Eke et al. 2011) such leakages none have yet to be truly tested or proven to work. Hence there is significant uncertainty related to structural trapping, which may lead to public acceptance problems. For example CCS projects have been stopped in Germany and the Netherlands because of such technical uncertainty and associated public acceptance problems (Terwel 2012).

Residual trapping is generally considered secondary to structural trapping in the importance for CCS projects. It is important with respect to preventing migration of CO₂ and if no caprock is proven or exists (Qi et al. 2009). In residual trapping the injected CO₂ displaces water in the reservoir when injected and a fraction of CO₂ is trapped by capillary forces. The process is analogous to the trapping of oil/natural gas during waterflooding in hydrocarbon reservoirs (Iglauer et al 2011a). The extent of residual trapping generally increases with higher values of γ and lower values of brine-CO₂-rock contact angles (much like structural trapping). It is further more a function of the pore morphology (Spiteri 2008), initial CO₂ saturation and rock porosity. Iglauer et al. 2011b further outlines capillary trapping capacity (C_{trap}) of porous rock and how it is a product of porosity and the residual nonwetting-phase (CO₂) saturation. They also grade rocks according to their worth for residual trapping of CO₂.

The two main difficulties with employing experimental work to measure the interfacial tension and the contact angle are partially contradicting results and accurately recreating the range of subsurface conditions. Molecular dynamics simulations offer an attractive method by providing a microscopic view which is not always attainable from experiments, but also the ability to predict behavior in conditions that cannot always be recreated by an experimental method.

Overview of work

The main content of this work is split into two main sections;

Further investigations with the fully coordinated alpha quartz surface in application to subsurface gas injection (part 1)

Iglauer et al. 2012 observed from their simulations that there is a strong contact angle increase (CO₂-water-quartz) with increasing pressure. It was also observed that increasing the temperature significantly reduces the contact angle, especially at low-intermediate pressures (1-10 MPa). The study further concluded that the influence of salinity, in form of the monovalent salt NaCl, has a minor effect on the contact angle. In this part of the work we will perform simulations with the same model used in Iglauer et al. (2012) and investigate the effects of divalent salts on the contact angle. Simulations on the influence of other gases, such as H₂S and N₂, on the water-quartz contact angle will also be explored.

Development of Hydroxylated alpha quartz surface (part 2)

The CO₂-water interfacial tension (γ) has been experimentally measured extensively and is considered a property well understood (Aggelopoulos et al. 2010, Chalbaud et al. 2009, Chun and Wilkinson 1995, Espinoza and Santamarina 2010, Georgiadis et al. 2010a, Georgiadis et al. 2010b, Georgiadis et al. 2011, Hebach et al 2002). γ has been successfully simulated with molecular dynamics by Iglauer et al. 2012 which reproduced the dependence of γ on pressure below the CO₂ saturation pressure at 300 K, and over predicted by ~20% at higher pressures. With respect to the contact angle (θ), experimental data measurements available from Chiquet et al 2007, Espinoza and Santamarina 2010, Mills et al 2011, Bikkina 2011, Kim et al 2012 and Broseta et al. 2012 have significant variations. Notably Iglauer et al. (2012) performed simulations on a fully coordinated surface with no silanol groups (Si-O-H) present on the surface. In experimental measurements however the quartz surface is covered with these silanol groups. This section of work focuses on hydroxylating the alpha quartz surface (adding these groups) and investigating how the contact angle varies on that surface.

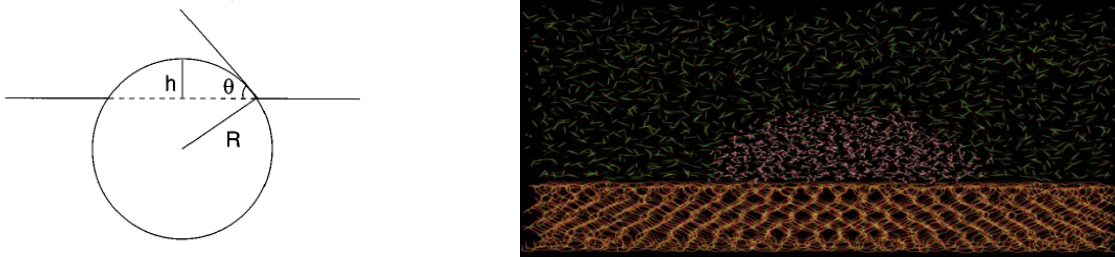


Figure 1: (left) Figure showing parameters measured to obtain contact angle with Bresme and Quirke 2000 method equation 9
 Figure 2: (right) Water droplet on fully coordinated quartz surface surrounded by CO₂

Table 1: Summary of significant previous work with respect to measuring the contact angle of quartz-water-CO₂. Measurements from Chiquet et al. 2007 and Mills et al. 2011 are representative of Reservoir Conditions. The cycle-effect observed in Bikkina et al. 2011 was explained with water-dehydration from the water surface by scCO₂ though these conclusions by the authors are still under question. All measurements are from experimental data apart from Iglauer et al 2012, which were obtained from molecular dynamics simulations.

Authors	Overview of Contact Angle Measurements
Chiquet et al. (2007)	θ increased from 22-38° with an increasing pressure of 1-9 MPa (T=308K, 0.2 M salt concentration)
	θ increased 5° with an increasing salinity of solvent from 0.2-1M solution
Espinoza and Santamarina (2010)	θ approximately constant at 40° with increasing pressures at intervals from 1-10 MPa (T=298K, 0.2 M salt concentration)
	θ increased 20° when 200g NaCl/kg water was used in the system compared to deionized water
Bikkina (2011)	Constant θ (T=298K, deionized water) with increasing P ressure
	θ between 25-30° for first CO ₂ exposure cycle and θ between 65-70° for second CO ₂ exposure cycle (3-20 MPa, T=298K)
Mills et al. (2011)	θ measured between 27-32° at 12.9 MPa (T=313.5K)
	θ was measured as 38-40° at 5.8 MPa (sub-critical CO ₂) but then at 27-38° at 13 MPa (super-critical CO ₂)
Kim et al. (2012)	Observed values as high as 80° on a siliceous micromodel after drainage with CO ₂ at 8.5 MPa (T=348K, 5 M salt concentration)
Broseta et al. (2012)	Measured drainage θ of approx. 35° and imbibition θ from 60-70° at pressures 1-10 MPa (T=282K, 0.8M salt concentration)
	Observed that hysteresis increases with Pressure
Iglauer et al. (2012)	Increasing contact angle from 0-82° with an increasing pressure of 0-19.5 MPa (T=300K)
	Increasing contact angle from 40-81° with an increasing pressure of 3-26 MPa (T=350K)

Further investigations with the fully coordinated alpha quartz surface in application to subsurface gas injection (part 1) Simulation Model Overview

Molecular dynamics simulations were first developed by Alder and Wainwright (1957) who first purposed the basic outline of the method. Rahman (1964) applied this approach to systems described by continuous potentials. Molecular Dynamics investigates the behavior of molecules in a system by using Newton's laws of motion to track the positions, velocities and forces between all of them. The forces between all the molecules in the system (known as the force field) are fitted to empirical measurements or quantum mechanical computations.

As previously stated simulations were performed with the same model used in Iglauer et al. 2012. Simulations were performed with the package DL_POLY 2.19. The TIP4P-2005 potential model was selected for water (Abascal and Vega 2005) and the EPM2 model for CO₂ (Harris and Yung 1995). Both of these models have been selected in previous simulation studies with both models showing good agreement with experimental data at elevated temperatures and high pressures (Nielsen et al. 2012, Biscay 2009 and Iglauer et al 2012).

An orthorhombic unit cell was periodically repeated to create a quartz slab. The slab was then equilibrated to create a quartz crystal with a fully coordinated surface (Si-O-Si bridged surface).

The force field parameters for the quartz atoms are given in table 2. The interatomic potential is in the form of a Coulombic potential and a Buckingham potential as given in equation (4):

$$U(r_{ij}) = \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}} + A_{ij} e^{-b_{ij} r} - \frac{C_{ij}}{r_{ij}^6} \dots \dots \dots (4)$$

$U(r_{ij})$ is the interaction energy between atoms i and j , q is the charge on each atom site, e is the electron charge, ϵ_0 is the vacuum permittivity and A_{ij} , b_{ij} and C_{ij} are constants taken from van Beest et al. 1990.

The interaction potential between the water, gas (CO₂, H₂S and N₂) and ions (Ca²⁺, Mg²⁺ and Cl⁻) was computed using Coulombic potentials and dispersion interactions. Dispersion interactions were included using a Lennard Jones (LJ) model show in equation (5):

$$U(r_{ij}) = 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} + \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) \dots\dots\dots(5)$$

Where ϵ is the interaction strength between the atoms, σ is the effective diameter of the atom and r_{ij} is the distance between the two atoms i and j . The Lorentz-Berthelot combining rules were used to obtain the interaction strength and effective diameter parameters between various atoms i and j (Hansen and McDonald 2006) with equations (6) and (7):

$$\sigma_{ij} = \frac{(\sigma_{ii} + \sigma_{jj})}{2} \dots\dots\dots(6)$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \dots\dots\dots(7)$$

The LJ parameters selected for the CaCl₂ were taken from Timko et al. 2011 which correspond to the CHARMM force field. The LJ parameters selected for the MgCl₂ were taken from Callaham et al. 2010 which experimentally validated their force field parameters by comparing Molecular Dynamics simulations with observations in the behavior of MgCl₂ in aqueous solution.

For H₂S a rigid body model was created based on the work of Shyamal 2003 which had a H-S-H angle of 91.5° and a H-S bond length of 1.365 Å. Shyamal 2003 performed isothermal-isobaric simulations (N,P,T) showing good agreement with coexistence experimental data. We used this fact to obtain the fluid pressure from the density of the simulated system (NIST 2012). Note that this H₂S model was further validated by Lopez-Rendon et al 2008 which from their simulations matched experimental results with respect to the solubility of H₂S and CO₂ in water.

N₂ was modelled as a rigid dumbell with bond length of 3.292 Å and LJ parameters taken from Kriebel et al. 1996. The model is in good agreement with experimental data at supercritical conditions but it is not as accurate in predicting the critical point (CP). However in the ranges of conditions considered in our simulations the model shows good accordance with the Equation of state (EOS) from Jacobsen et al. 1986, and therefore is accurate for our investigation.

Table 2 Outline of all the Force Field parameters taken from various sources, see in the above text

<i>Buckingham potential parameters</i>			
Interaction	A(ij) (kJ/mol)	b(ij) (Å⁻¹)	c(ij) ((kJ/mol)x(Å⁶))
O-O	1.34E+05	2.76	1.69E+04
Si-O	1.74E+06	4.873	1.29E+04
<i>Lennard Jones potential parameters</i>			
Site	ϵ (kJ/mol)	σ (Å)	q (e⁻)
O (water)	0.77502	3.1589	0
M (water)	0	0	-1.1128
H (water)	0	0	0.5564
C (CO2)	0.23391	2.757	0.6512
O (CO2)	0.66947	3.033	-0.3256
Si	0.5335	3.795	2.4
O (quartz)	0.6487	3.154	-1.2
Ca2+ (CaCl2)	0.50208	2.734	2
Cl- (CaCl2)	0.666	4.91776	-1
Mg2+ (MgCl2)	3.661	1.06	2
Cl- (MgCl2)	0.4184	2.4192	-1
S (H2S)	2.0789	3.72	-0.248
H (H2S)	0.0324	0.98	0.124
N (N2)	0.3019	3.2973	0

17Å was set as the cut off for Van der Waals interactions. The Ewald summation method (Ewald et al. 1921) was used to compute long range columbic interactions. Simulations were performed with periodic boundary conditions in all but one of the box's directions, along z-axis. Instead a soft repulsive potential set in the x-y plane above the quartz surface. The force is harmonic in the form of equation (8):

$$f_{rep} = -k(z - z_0) \dots\dots\dots(8)$$

With $k=1$ kJ/mol (force constant) and z_0 is z coordinate where the repulsive potential is set. For these simulations it was located 55Å above the quartz surface. The position allows the water droplet's contact angle not to be affected by the repulsive

wall.

The timestep for all simulation runs was set to 0.002 picoseconds (ps). The number of equilibration steps set to 5×10^4 steps and the production steps being 0.5×10^6 steps.

To evaluate the contact angles the method reported by Bresme and Quirke 2000 was applied. From the parameters measured (see figure 1), equation 9 is used to calculate the contact angle:

$$\cos(\theta) = 1 - \frac{h}{R} \dots \dots \dots (9)$$

Where h is the height of the droplet and r is the radius.

Simulation of Divalent Salts (CaCl₂ and MgCl₂)

Previously Iglauer et al. 2012 measured contact angles from molecular dynamics simulations with varying NaCl concentration from 1M to 4M at 300K/4MPa. The conclusion was drawn that salinity has a minor effect on the water’s interfacial structure as well as the contact angle. Experimentally the effect of salinity (NaCl) on the water contact angle is inconclusive. Chiquet et al. 2007 measured a small decrease in the contact angle with increasing salinity. Espinoza and Santamarina 2010 reported very significant decreases in contact angle with increasing NaCl concentration. To the author's best knowledge no experimental work or molecular dynamics simulation have been performed to see how other salts, in this case divalent salts in the form of MgCl₂ and CaCl₂, affect the contact angle on a quartz surface. Both CaCl₂ and MgCl₂ are consistently found in reservoir formation water.

Simulations were first performed at 1M and 4M conditions for both CaCl₂ and MgCl₂. The molarity of water was varied by randomly removing water molecules in the droplet and replacing them with ions. Taking the 4M CaCl₂ case as an example there was a total of 815 water molecules in the droplet with 59 CaCl₂ ion pairs (59 Ca²⁺/118 Cl⁻ ions) also present. The temperature was set at 300K and the number of CO₂ molecules in the system was set to 525. This was so the pressure was low to be compared to the results from Iglauer et al. 2012.

The results of these simulations showed there was a small but distinguishable difference in contact angle between mono- and divalent cations (that is NaCl and CaCl₂/MgCl₂ respectively).

From the water density profile along the z-axis it is clear that the droplet’s interfacial structure change with CaCl₂ and MgCl₂ is minor (see figure 4) which is a similar finding to how NaCl affected the water’s interfacial structure in Iglauer et al 2012.

Iglauer et al. 2012 showed that pressure is very important in terms of having an impact on the contact angle. To investigate the significance of these angle measurements at storage pressures in the subsurface the simulations for 1M CaCl₂ were repeated at higher pressures between 10-15MPa.

The results from these simulations showed that at typical subsurface pressures the divalent salts have negligible effect (see figure 3) on the contact angle, much like which was concluded with NaCl in Iglauer et al 2012.

It suggests that for CCS projects to estimate the amount of residual trapping and the caprock integrity, with respect to knowledge of the capillary entry pressure, knowing the composition of the brine is relatively unimportant.

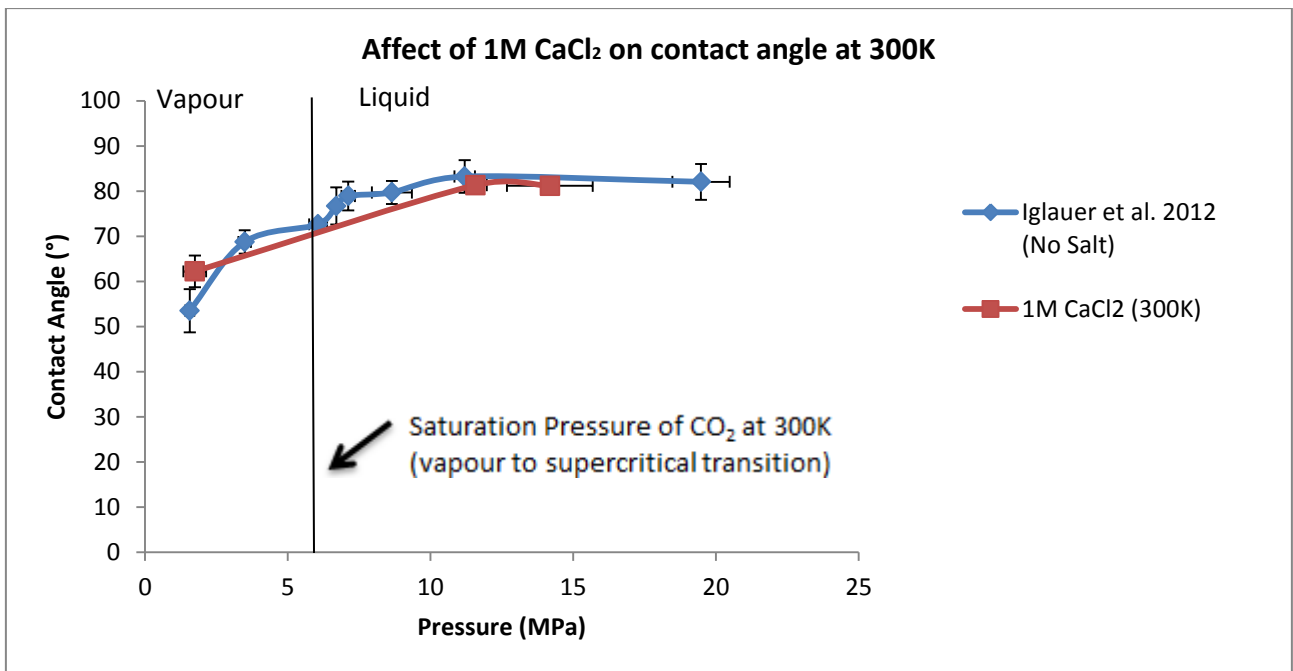


Figure 3: Contact angles results from simulations of Iglauer et al 2012 with no salt and at 300K compared to these simulations with 1M CaCl₂ at 300K.

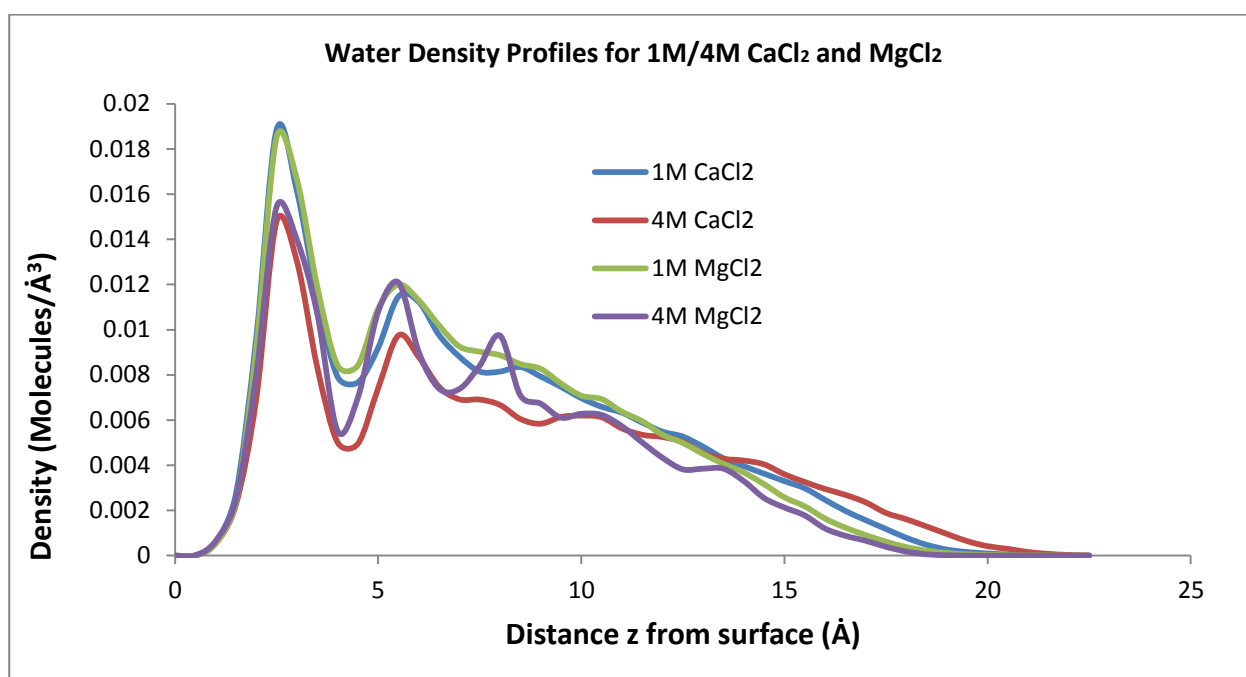


Figure 4: The water density profiles above the surface of the fully coordinated quartz at approximately 1.6MPa/300K for 1M/4M CaCl₂/MgCl₂

Simulation of N₂/Water/quartz system

It has been proposed by Dr Iglauer's group, along with their CarbonNet project partners, that Nitrogen (N₂) could be a potential gas for injection into aquifers. This would be done to test a potential site for the use of it in a CCS project and N₂ could then be used for leak detections. Nitrogen gas injection is also used for EOR techniques (Lake 1989) so understanding its interfacial behavior with quartz in the subsurface is an important issue.

These simulations have been conducted to give an initial insight into how similar water/N₂/silica contact angles compare to water/CO₂/silica contact angles. The results may be able to be compared to experimental results in the near future as no experimental results have been found to compare to.

The highest pressure the nitrogen/water/silica system was simulated at was 12.1MPa/350K (table 3). All results up to this pressure lead to a completely water wet silica surface (0 contact angle). Though simulations should be performed at higher pressures to confirm N₂ as completely non-wetting to the quartz surface, the initial results suggest that conclusion.

N₂ is much less wetting of the fully coordinated quartz surface compared to CO₂. This is likely due to the lower van der Waals interactions that N₂ processes. From table 2 the interaction strength parameter (ϵ) of oxygen in CO₂ is 0.66947 kJ/mol which around twice that of nitrogen in N₂ (0.3019 kJ/mol). This corresponds to two effects. The first is that at similar pressures N₂ is at a much lower density than CO₂. This corresponding to less molecules of N₂ competing with the water for the surface of the fully coordinated quartz. The second is that there is less an attraction between the fully coordinated quartz surface and N₂ in comparison to CO₂. Both these effects significantly decrease its wettability.

These initial results from the simulation of N₂/water/silica contact angle suggest that use of N₂ to test for the extent of residuals trapping would be a poor comparison. The test would also significantly overestimate the capillary breakthrough pressure of the caprock with respect to structural trapping. It should be noted that N₂ may be a good representation to test other aspects of structural trapping and other trapping mechanisms, except residual trapping; however that research is out of the scope from this discussion.

Table 3: Summary of results from simulations of N₂/H₂O/fully coordinated quartz systems. Simulations were run for a total of 5x10⁴ equilibration steps and 5x10⁵ productions steps.

Pressure (Mpa)	error	Temperature (K)	Angle	error	Comments
10	0.4	300	0	N/A	Water wet surface
12	0.6	350	0	N/A	Water wet surface

Simulation of H₂S/Water/quartz system

To the best of the author's knowledge only Shah et al 2008 have experimentally measured the water-wettability of caprock minerals in the presence of H₂S. They measured a water contact angle of 42-45° at pressures ranging from 0.6-12.5MPa at 323K with 0.08M NaCl concentration on a quartz surface.

The simulations in the present work were performed at 350K to compare to the contact angle measurements from the simulations of Iglauer et al. 2012 of CO₂/water/quartz at 350K. The results from these simulations suggest that the H₂S/H₂O/quartz contact angle is larger than the corresponding CO₂/H₂O/quartz contact angles at small and intermediate pressures (see figure 5). The simulation results however did not match with experimental results obtained by Shah et al. 2008. The reason for such differences may be due to the same explanation provided by Iglauer et al 2012 on why their simulated CO₂/water/quartz contact angles differed so much from experimental data. They suggested the surface's degree of roughness is important and how the surface becomes chemically modified during cleaning and the actual experiment itself. In these simulations we have a fully coordinated alpha-quartz surface. However, a quartz surface in a reservoir contains silanol groups. This may explain the difference in contact angle. It also further motivates the second part of this report which investigates the construction of the hydroxylated surface to see how contact angle is affected by the silanol groups.

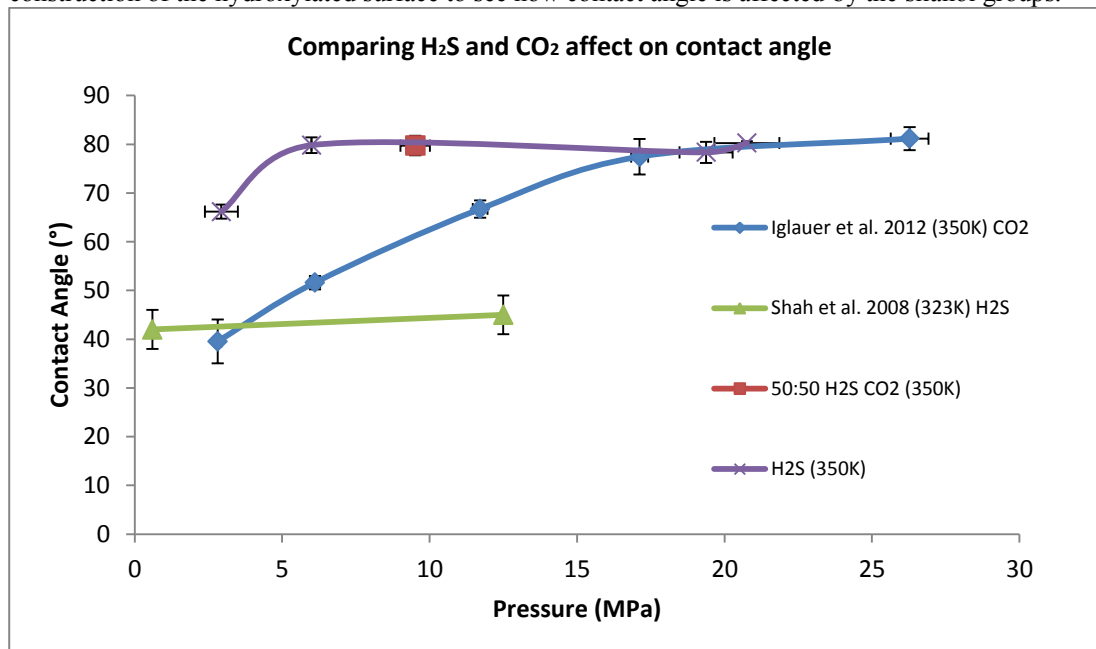


Figure 5: Contact angle of H₂S/H₂O/quartz from simulations (this work) compared to experimental data from Shah et al 2008 and simulations of the CO₂/H₂O/quartz contact from Iglauer et al 2012.

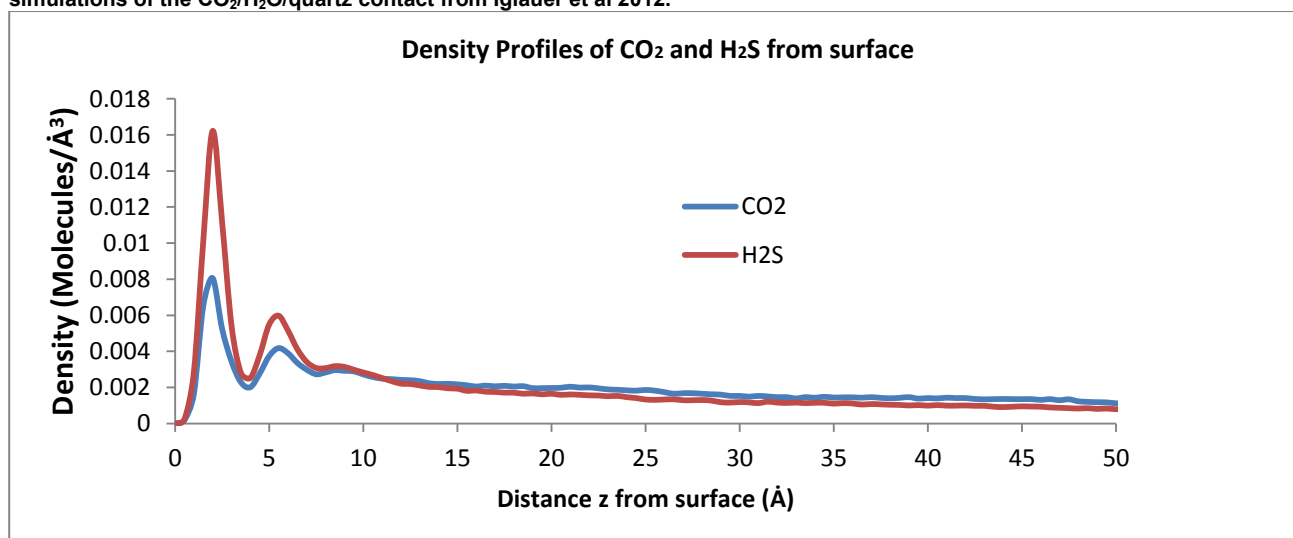


Figure 6: Density profile of CO₂ and above quartz surface from the simulation of 50%H₂S/50%CO₂/water/quartz contact angle

A simulation was then run with 50mol%H₂S:50mol%CO₂/H₂O/quartz to see how the contact angle compared to simulations of a 100%CO₂/H₂O/quartz system and a 100%H₂S/H₂O/quartz system. It could also be used to compare the wettability of H₂S and CO₂ to the quartz surface. As can be seen from Figure 6 the surface density of H₂S is larger than the surface density of

CO₂. This suggests that H₂S has a larger affinity for the surface therefore helping to explain why H₂S/H₂O/quartz contact angles are larger than the corresponding CO₂/H₂O/quartz contact angle.

This observation of H₂S being more wetting of the crystal surface is somewhat consistent with experimental measurements on quartz and completely consistent with measurements on other surfaces, namely mica crystal and Rousee caprock. Comparing measurements from Broseta et al 2012 with Shah et al. 2008 on quartz; the drainage contact angle of CO₂/H₂O/quartz was approximately 35° at 0.1-10MPa/282K compared to drainage contact angles of H₂S/H₂O/quartz being 42-45° at 0.6-12.5MPa/323K. Shah et al 2008 observed a significant increase in drainage and imbibition contact angles when comparing the contact angle of CO₂/H₂O to H₂S/H₂O on a mica crystal. For example the drainage water contact angle measurement on mica with CO₂ present at 1MPa/308K was 28°. Compare this to a drainage contact angle of 62° with the presence of H₂S at 1.5MPa/323K.

The pressure of 50mol%:50mol% H₂S:CO₂ was approximated as 9.5MPa (see figure 5) from a form of Dalton's law;

$$P_{total} = \sum_{i=1}^n p_i \dots\dots\dots(10)$$

$$P_{total} = EOS_{CO_2}(\rho_{CO_2}) + EOS_{H_2S}(\rho_{H_2S}) \dots\dots\dots(11)$$

Equation 10 being Dalton's law where n is the number of different molecules, P_{total} is the Pressure of the system and p_i is their respective partial pressure. Equation 11 shows how the pressure of this system was approximated. EOS stands for the equation of state and ρ being the density. One limitation with this pressure approximation is the assumption that the system behaves as an ideal mixture. To calculate the actual pressure of this simulation canonical simulations (N,P,T) of 50mol%:50mol% H₂S:CO₂ would be required. This is beyond the scope of this study.

Results from the simulations of H₂S/H₂O/quartz contact angle measurements suggest that subsurface H₂S injection has less residual trapping and there will be a lower capillary break though pressure with respect to structural trapping. The simulations suggest that this difference is most apparent at low/intermediate pressures (<20MPa) and much less apparent at higher pressures (>20MPa).

We note here that H₂S is a toxic and flammable gas. Exposure to concentrations exceeding 10ppm for more than 8 hours is considered above the permissible exposure limit set by the occupational safety and health administration (OSHA) (U.S. Department of Health and Human Services 2006). It seems somewhat surprising that the general public is less concerned about H₂S with respect to subsurface injection for storage compared to CO₂ in CCS projects.

Development of Hydroxylated alpha quartz surface (part 2)

Simulation Model Overview and creating the crystal surface

With respect to the model of CO₂ and H₂O selected, the timestep, the cutoff for Van der Waals interactions and the method to compute long range Coulombic interactions, these are the same as those reported in part 1 of this report. Simulations were not performed with periodic boundary conditions in the z-axis. Instead a soft repulsive potential (k=1kJ/mol) set in the x-y plane 64.5Å above the quartz surface (equation 8).

An orthorhombic unit cell was periodically repeated to create a quartz slab. The slab was then equilibrated at 1K to create an ordered quartz crystal with a fully coordinated surface (Si-O-Si bridged surface). The top surface was hydroxylated by deleting bridging oxygen atoms and then capping the newly under coordinated silicon atoms with oxygen atoms 1.61Å directly above them. The average Si-O bond length was 1.61Å in the quartz crystal and so that length was selected as the Si-O bond length in the Silanol groups (Si-O-H). This was also the same as the Si-O bond length used in Lee and Rossy 1994.

A Si-O-H bond angle of 122.5° was used with an O-H bond length of 0.975Å. These two parameters were taken from the work of Lopes et al 2006 which developed an empirical force field for silica with application to the quartz-water interface. This bond angle and O-H bond length was also used in the work of Liu et al 2010. This bond length and angle was consistent with Cruz-Chu et al 2006 who modelled the hydroxide (O-H) in silanol on the TIP3P model of water. The O-H bond length was also close to the value used by van Duin et al 2003 in their model. The hydrogen atoms were randomly orientated relative to the bonding oxygen by selecting a random number between 0-2π (φ) and then using the equations (12-14) to convert spherical coordinates into cartesian (θ=57.5°, r=0.975Å)

$$x = r \sin \theta \cos \varphi \dots\dots\dots(12)$$

$$y = r \sin \theta \sin \varphi \dots\dots\dots(13)$$

$$z = r \cos \theta \dots\dots\dots(14)$$

The force field parameters for the quartz atoms were the same as section 1 which notably were taken from the well-test model (BKS) of bulk silica created van Breest et al 1990. Following the approach of Hassanali and Singer 2006 the hydrogen atoms were assigned a charge of +0.6 to ensure charge neutrality of the under coordinated surface. The LJ parameters for all the atoms were the same as in section 1 with the van der Waals interactions for the hydrogen in the silanol groups set to zero, like hydrogen is in the model used for water.

Zhuravelv 2000 provides a good review of the extensive experimental work that studied the hydroxylation and rehydroxylation that takes place at a silica-water interface. It states that the amorphous silica hydroxylated to the maximum degree is considered to be a physico-chemical constant of 4.6 OH/nm². The Zhuralvel model has stood up well to solving various applied and theoretical problems with respect to the hydroxylated silica surface. Surfaces with varying degrees of hydroxylation were formed (4.5-1.7 OH/nm²). A block of 1000 water molecules was set at 3Å above the surface and a

simulation run for 5×10^3 equilibration steps and 5×10^4 production steps. This was performed so the block of water would initially wet the surface. CO₂ molecules were then added to the system and the simulation run for up to 5×10^4 equilibration steps and 4×10^5 production steps. Due to the surface not being large enough (98 Å by 102 Å) water molecules were first deleted from near the boundaries of the block. Water molecules were then secondly removed from the droplet itself so there were equally 700 water molecules left in the simulation box. The simulations were then run for a further 4×10^4 equilibration steps and 4×10^5 production steps to obtain the equilibrium water contact angle.

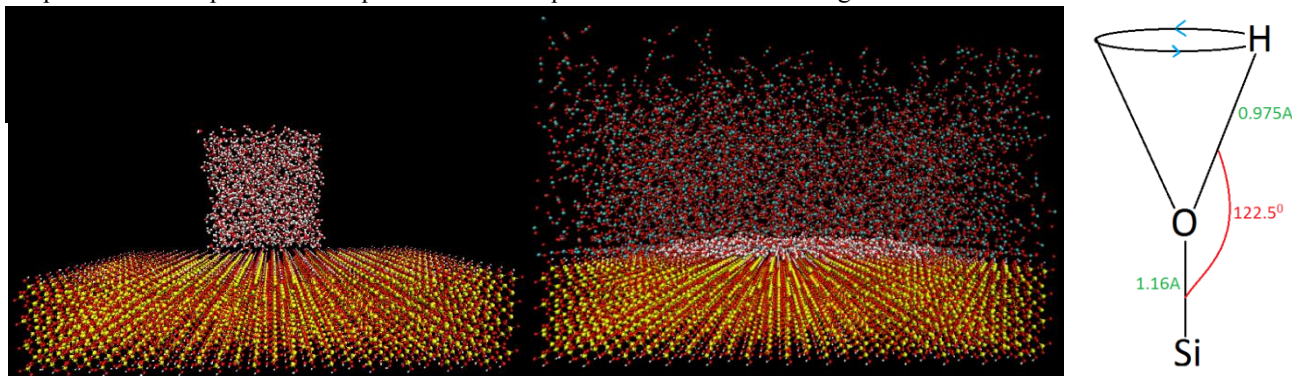


Figure 7: (left) Block of 1000 water molecules set approximately 3Å above the surface.

Figure 8: (middle) Simulation box after 5×10^4 equilibration steps and 0.5×10^6 production steps where block of water has wet the surface and then CO₂ molecules added to the box.

Figure 9: (right) Schematic of putting the hydroxyl group on the dangling silicon atoms post deletion of bridging oxygen on the surface.

Discussion of other silica models tested

Various surfaces with different force field parameters were tested throughout this study. Work from Liu et al 2010 was attempted to be recreated with instead increasing the surface hydroxyl-group concentration from 1.6 OH/nm² (what was used by the authors) to 4.5 OH/nm² (close to the maximum silanol density on an actual silica surface). The angles obtained by Liu et al 2010 could not be recreated. Our results showed the model of the surface to be much less wetting than the fully coordinated surface simulated by Iglauer et al 2012. Such difference is most likely due how the hydroxyl groups were distributed on the silica surface. In Liu et al 2010 the Hydroxyl groups were more uniformly distributed on the surface. In our recreation of their model the hydroxyls are more non-uniformly distributed to be more realistic of an actual hydroxylated quartz surface. Note that Liu et al 2010 contact angle measurements were not consistent with Iglauer et al 2012. Liu et al 2010 showed through simulation that the fully coordinated quartz surface would be CO₂ wetting at pressures above 20MPa. Iglauer et al 2012 however measured contact angles of approximately 80° at similar pressures. Liu et al 2010 contact angles for the hydroxylated quartz surface were closer to the results obtained by Iglauer et al 2012 but even this was brought into question. Liu et al 2010 obtained a contact angle of just below 60° at atmospheric pressure. Iglauer et al 2012 however obtained a contact angle closer to 0°. The conclusion is that the model in Liu et al 2010 is not an accurate representation of the hydroxylated or the non-hydroxylated silica surfaces.

Force field parameters taken from Hassanali and Singer 2006 were then simulated with the Si-O-H bond orientation varied by using the provided truncated Vessal angle potential setting the Si-O-H bond to 64°. The surface was completely wetting of water (corresponds to a contact angle of 0°) even at high pressures >15MPa. The force field parameters were then used in a simulation of the frozen fully coordinated surface with water and CO₂ (pressure approximately 10MPa with temperature 300K). The surface was completely wetting of water. This suggested that the model was incorrect by not matching previously simulated data from the fully coordinated surface from Iglauer et al 2012.

Cruz-Chu et al 2008 parameters for all the intermolecular interactions were not used due to how they were optimized. The contact angle of water on the surface was matched to equation (15):

$$\cos \theta = 0.257 \alpha_{\text{SiOH}} + 0.743 \dots \dots \dots (15)$$

Where α_{SiOH} is the number of OH per nm² divided by 4.6 OH/nm² (the maximum silanol surface density). Equation 15 was taken from the heuristic relationship between the water contact angle and the concentration of silanols in polished silica plates found in Lamb et al 1982. This relationship is not consistent with the findings of the Iglauer et al 2012 which simulated a completely wet surface of the fully coordinated surface ($\alpha_{\text{SiOH}}=0$) at vacuum pressure. The relationship that equation 15 purposed is felt to be a large over simplification based on more recent experimental measurements of the water/CO₂/quartz contact angle.

Validity of the Hydroxylated quartz surface model

From investigations into other models for the hydroxylated quartz surface, the current model was considered the best representation. This was due to the force field parameters of bulk silica being well tested by van Breest et al 1990 and the fully coordinated form of the model reproducing the experimental interfacial tension measurements relatively successfully (Iglauer

et al 2012). By treating the hydrogen atoms on the silanol group much like Hydrogen in water, this was a very similar to the approach of Cruz-Chu et al 2006.

The charges of the silicon, oxygen and hydrogen atoms used in Lopes et al 2006, Cruz-Chu et al 2006 and de Leeuw et al 1999 was not used as it did not form a charge neutral quartz crystal. Cruz-Chu et al. 2006 method of assigning charge through various equations (clearly outlined in their publication) was avoided to keep the model relatively simple and mainly so different degrees of hydroxylation could be studied efficiently.

The frozen fully coordinated silica surface was simulated at a pressure of 10MPa at 300K. This was to investigate the effect of a lack of roughness and a lack of disorder on the surface. The wettability increased significantly with a contact angle of 55° compared to the results of Iglauer et al 2012 at the same pressure and temperature which measured an angle of 80°.

Though this decrease in the water contact angle was not enough to explain the higher wettability of the hydroxylated surface compared to the fully coordinated surface, it did suggest further modelling of the hydroxylated quartz surface should incorporate more disorder on the surface. The high order of the fully coordinated surface increased the degree of Hydrogen bonding between the water and the bridging oxygen atoms in the fully coordinated quartz surface. This explains the increase in wettability. However in the hydroxylated quartz surface simulations the hydroxyl groups, which are randomly orientated; dominate the hydrogen bonding therefore meaning that increasing disorder in the hydroxylated quartz surface may not have as much a significant impact. See figure 14 for further comments.

To investigate the consistency of our model the 1.7 OH/nm² hydroxylated silica surface was simulated with just CO₂ molecules present and separately simulated with 5191 water molecules placed approximately 3Å above the surface. These two simulations were repeated with the fully coordinated quartz model from Iglauer et al 2012 (used in part 1 of this report) and the frozen fully coordinated quartz surface. All these simulations were run for a total of 2x10³ Equilibration steps and 2x10⁴ Production steps. The results were compared with the results from Notman and Walsh 2009, Qin et al 2008 and Lee and Rossky 1994 which had constructed models for the hydroxylated quartz surface (see figures 10-16)

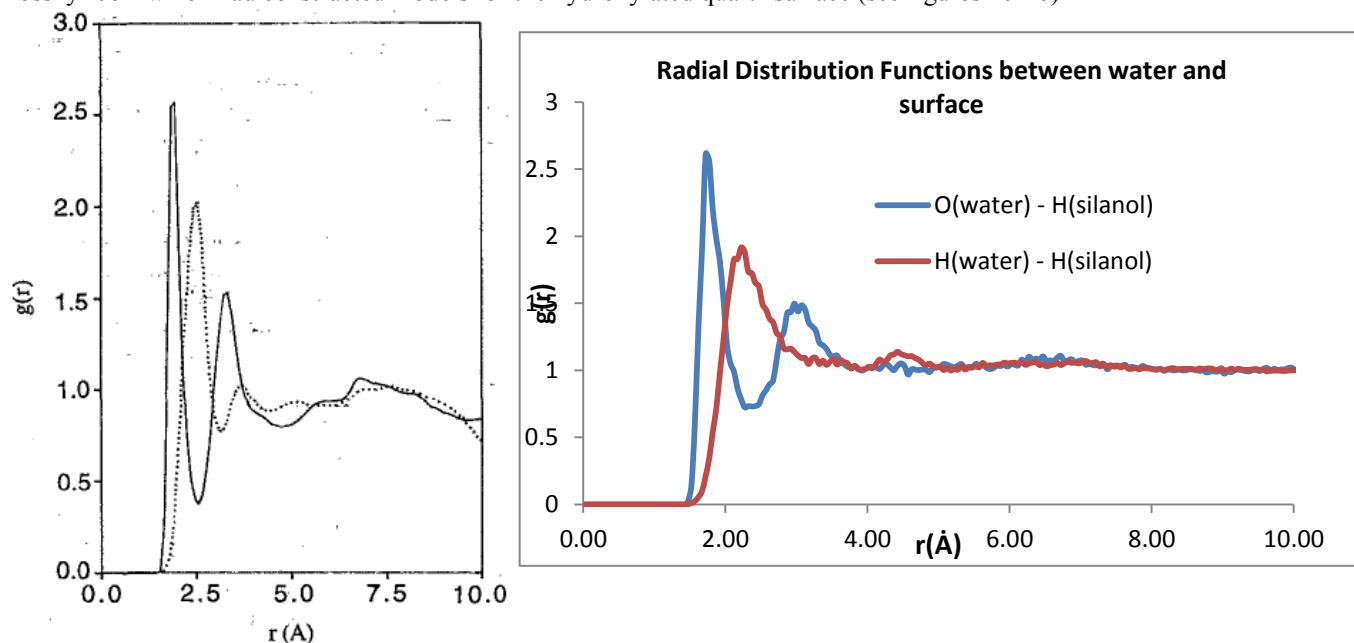


Figure 10: (left) radial distribution functions for O(water)-H(silanol)(full line) and H(water)- H(silanol)(dashed line) from Lee and Rossky 1994.

Figure 11: (right) radial distribution functions for O(water)-H(silanol) and H(water)- H(silanol) from this work

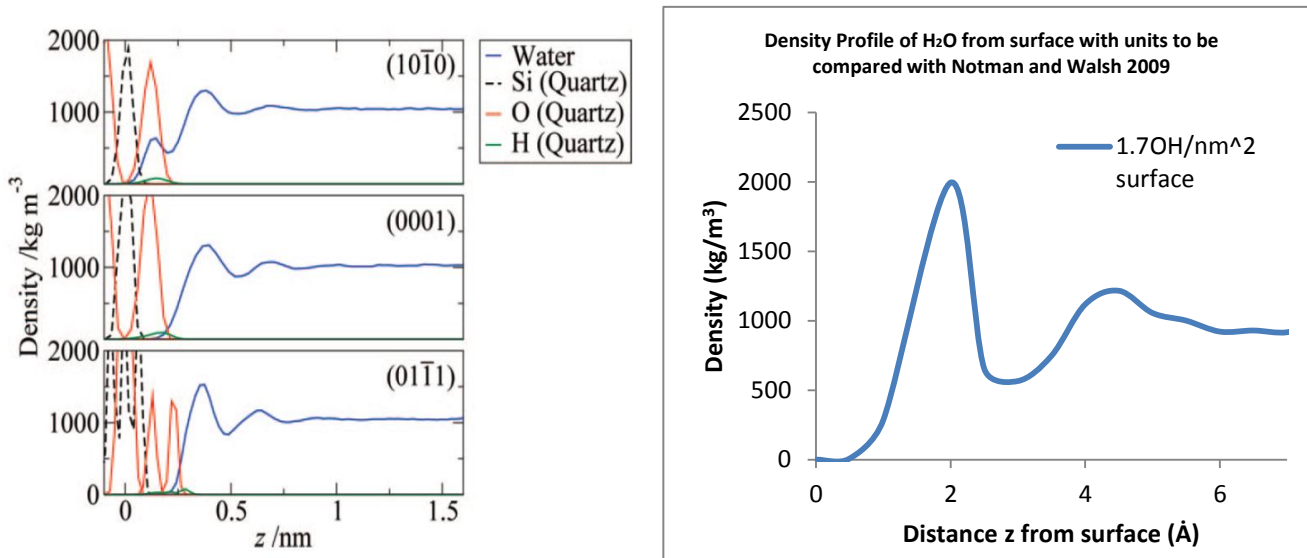


Figure 12: (left) Density profiles of various hydroxylated quartz surfaces from Notman and Walsh 2009.
 Figure 13: (right) Water density profile (z-direction) on the hydroxylated surface from this work.

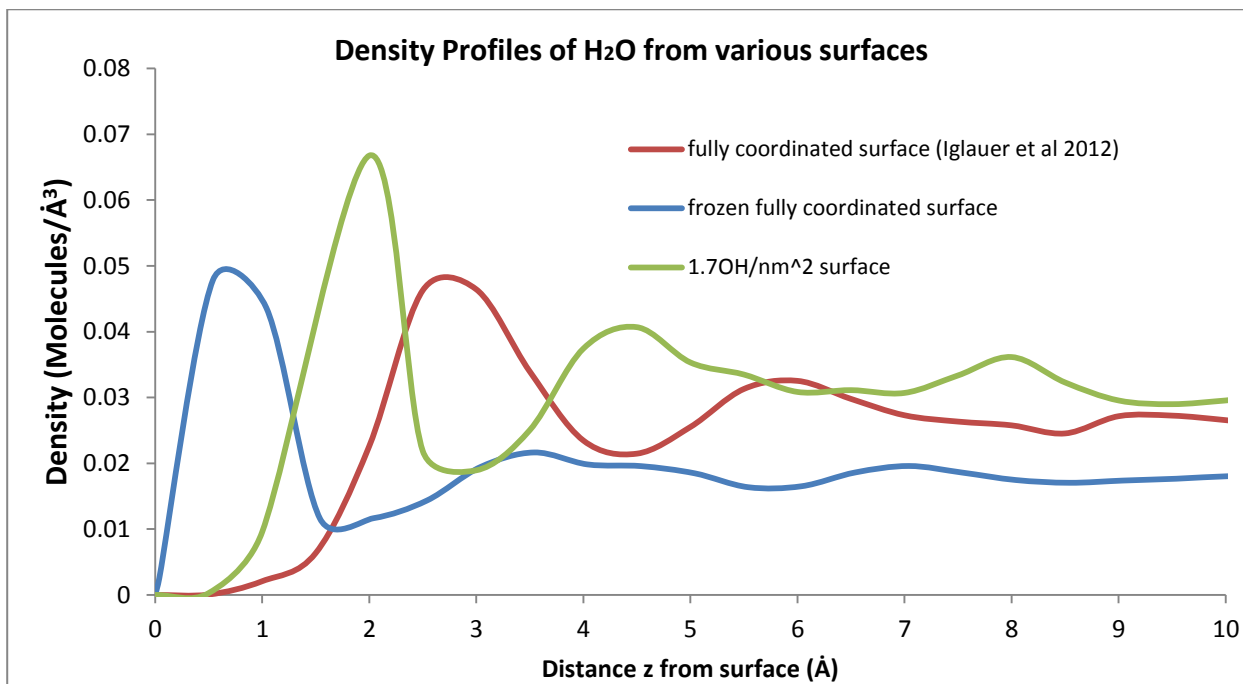


Figure 14: Water density profiles (z-direction) on the hydroxylated surface, fully coordinated silica surface from Iglauer et al 2012 and the frozen fully coordinated surface. Notice how both fully coordinated surfaces have approximately the same maximum density of water at their surface however with the frozen surface form the water penetrates much closer to the surface atoms. This perhaps causes a distortion in the droplet shape leading low contact angles being measured.

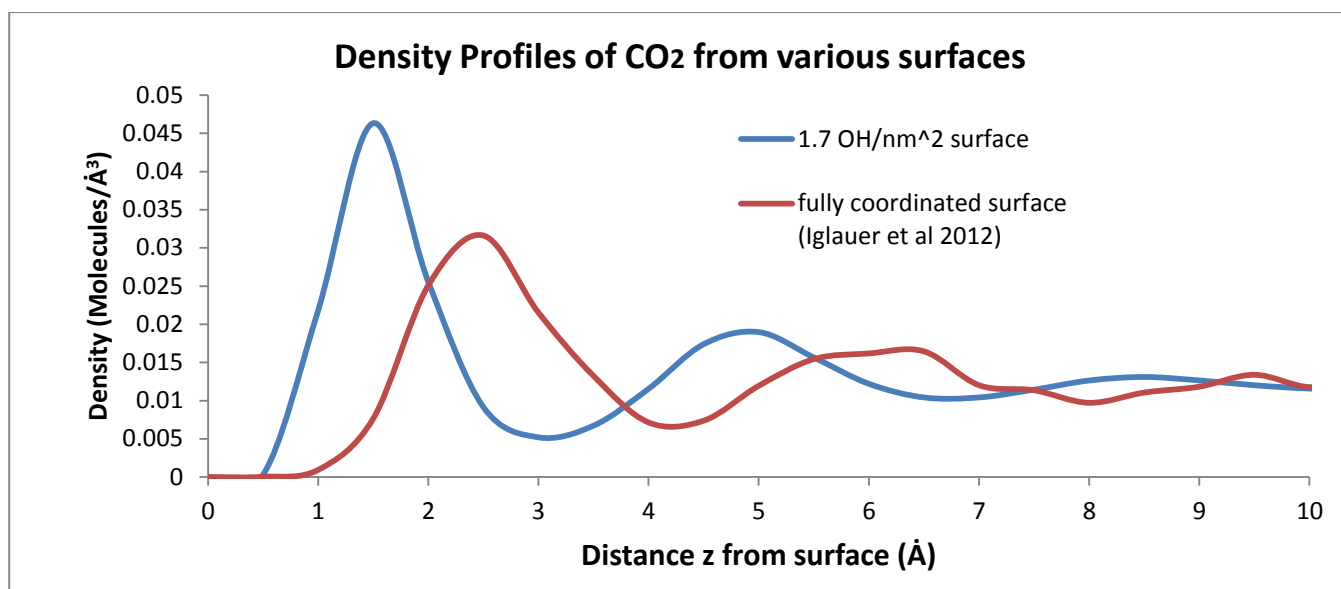


Figure 15: Density profile of CO₂ (along z-axis) on Hydroxylated quartz surface (blue) and on the fully coordinated quartz surface from Iglauer et al. 2012 (red).

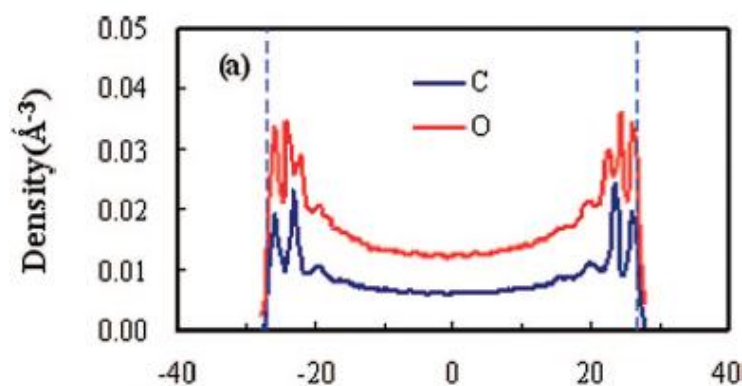


Figure 16: Taken from Qin et al 2008 showing density distribution of CO₂ in silt pores between two hydroxylated crystalline silica surfaces. The dashed blue line indicates the position of the surfaces in the pore

The concentration of OH/nm² on the quartz surface should be considered when comparing the hydroxylated quartz model to the other models. On the surface Lee and Rosicky 1994 had a concentration of 4.6 OH/nm², Qin et al 2008 had a concentration of 1.9 OH/nm² and Notman and Walsh 2009 did not clearly state the concentration of OH on the surface.

From considering this and analysing the comparisons between this model and others of the hydroxylated quartz surface we can observe that H₂O absorbed onto the hydroxylated quartz surface to a larger extent than the model used Lee and Rosicky 1994. CO₂ is absorbed onto the hydroxylated surface to a larger extent than the model created by Qin et al 2008. Qin et al 2008 used molecular dynamics simulation to investigate the interaction between supercritical CO₂ and modified silica surfaces. One of their main observations was how the hydroxylated silica surface absorbed more strongly with the supercritical CO₂ in comparison to the silylated surface. This was due to Hydrogen bonding interactions between the OH and CO₂ molecules. This was consistent with our observations which showed a large increase in absorption of CO₂ in the supercritical state.

Contact angles with varying Pressure and Hydroxyl concentration on the surface

The 4.5 OH/nm² surface was simulated at a pressure up to approximately 10MPa at 300K. The 3.7 OH/nm² surface was also simulated at a pressure up to 10MPa at 300K. Finally the lowest concentration of hydroxide on the surface was simulated (1.7 OH/nm²) at a pressure up to 12MPa at 300K.

As can be seen from figure 18 there is a significant decrease in the water contact angle compared to the work from Iglauer et al 2012 which performed simulations on a fully coordinated quartz surface.

From figure 17 it is clear that the contact angles from the hydroxylated quartz surface are closer to the values obtained from the range of experimental data available than the contact angles obtained by Iglauer et al 2012. Increasing the concentration of hydroxylation on the surface from 1.7-4.5 OH/nm² at approximately 10MPa/300K has an effect of decreasing the contact angle

by approximately 10°. Increasing the concentration of hydroxylation on the surface from 3.7-4.5 OH/nm² however has a negligible effect on the contact angle.

This suggests that changes in OH surface concentration changes the contact angle but does not explain the full variation in experimental results of the water contact angle on quartz. It has to be considered that in these simulations all the silanols were fully protonated. Silanol groups can further dissociate to form Si-O⁻. This may affect the contact angle significantly and may explain experimental measurements of a lower contact angle.

In the future to measure lower contact angles a larger surface would be more advisable. In these simulations the block had dimensions of 98x102Å. At lower contact angles the droplet starts to spread beyond the boundaries making the measurement of the contact angle unattainable as the surface then has to be considered completely wetting. This was a problem when simulating lower pressures in this investigation.

Another important consideration is how valid it is to compare many of the experimental measurements published with the molecular dynamics simulation results. In experimental measurements hysteresis is observed frequently with respect to drainage and imbibition contact angles. Hysteresis with respect to contact angle is believed to be due to fluid metastable states, adsorption of some fluid components and substrate chemical and/or geometrical heterogeneities (Broseta et al. 2012). In this type of molecular dynamics simulation the system reaches equilibrium and so many of these phenomenon cannot be observed. This also shows the power of molecular dynamics simulation as a method for what is desirable is to obtain is the contact angle of the CO₂/water/quartz in the subsurface.

Assuming this model of hydroxylated quartz is considered to be accurate it shows that the contact angle in the subsurface of CO₂/water/quartz to be approximately 35° at 10MPa/300K for high concentrations of OH on the quartz surface (3.7-4.5 OH/nm²) and at around 42° for lower concentrations of OH on the surface (1.7 OH/nm²). This means that compared to the fully coordinated surface there is a larger amount of residual trapping and a higher capillary breakthrough pressure with respect to structural trapping.

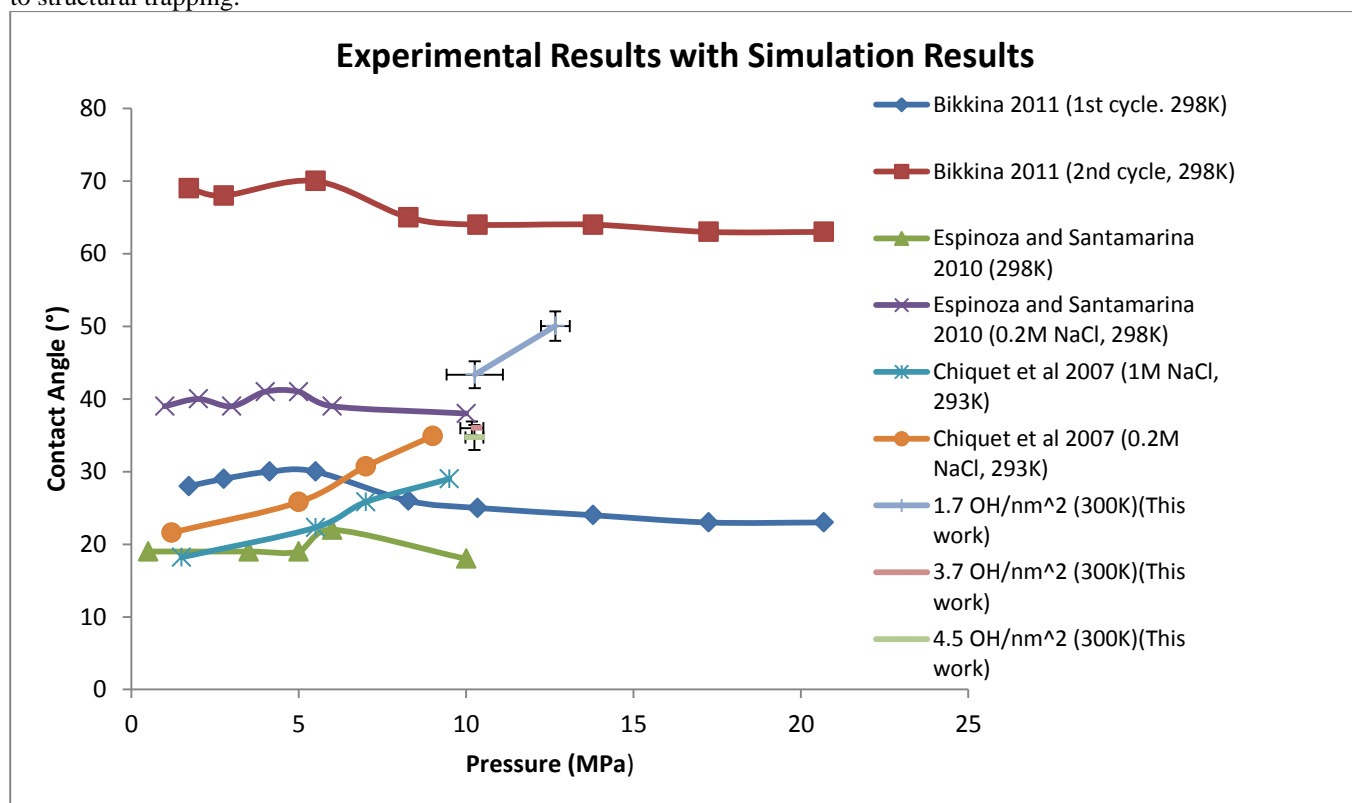


Figure 17: Comparing the experimentally obtained CO₂/H₂O/quartz contact angle with the results from these simulations on the hydroxylated quartz surface

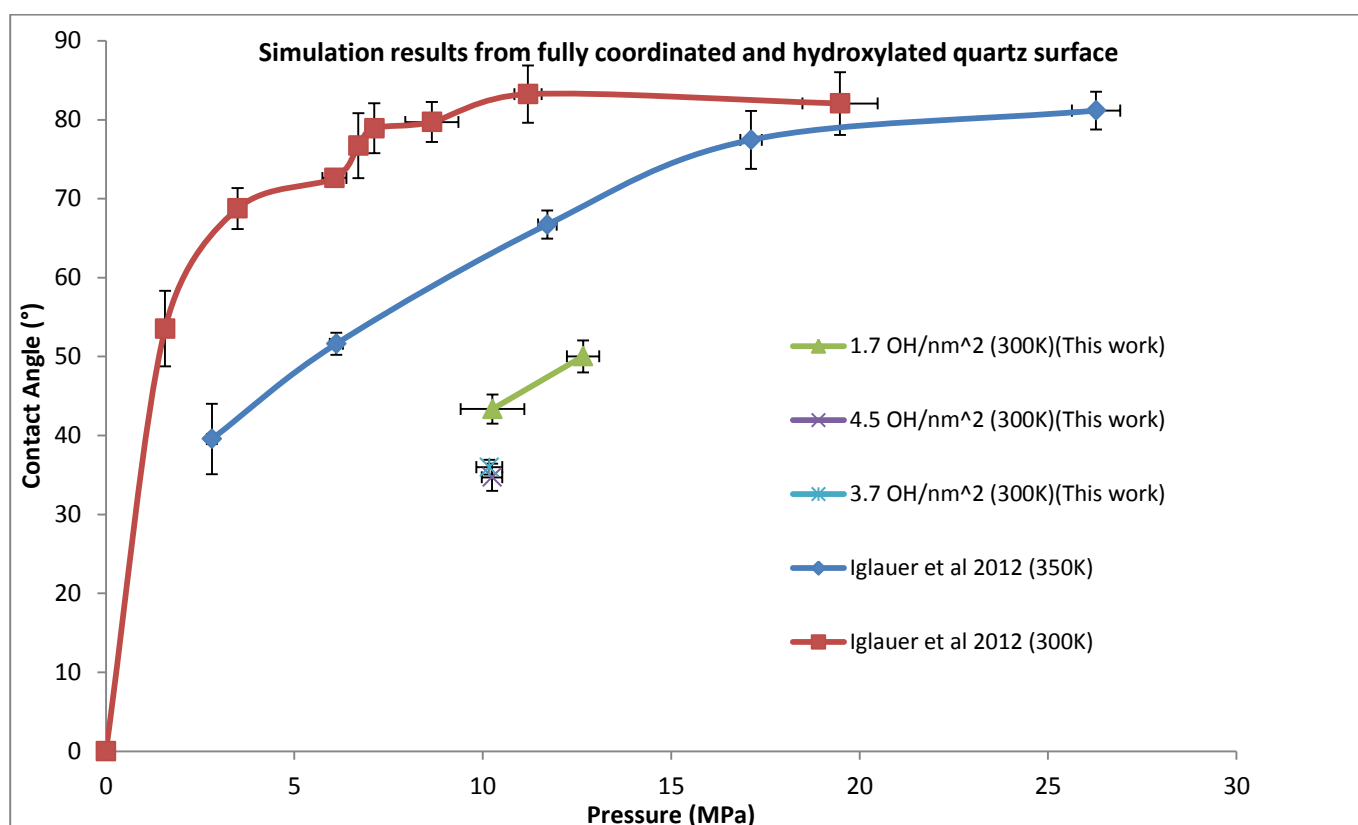


Figure 18: Comparing simulated contact angles of CO₂/H₂O/fully coordinated-quartz (Iglauer et al 2012) with the results from these simulations on the hydroxylated quartz surface

Conclusions and recommendations

We present here further findings on simulations from the fully coordinated α -quartz surface taken from Iglauer et al 2012 and a development of a hydroxylated α -quartz surface. By modelling the contact angle on hydroxylated quartz the results suggest that there will be significantly more residual trapping and more effective structural trapping when quartz is in its hydroxylated form in the subsurface. Though molecular dynamics simulation is a powerful method to recreate wide ranging subsurface conditions and to better understand experimental results with respect to interfacial interactions, it does not model quantum effects (any possible chemical reactions that may take place between the molecules).

We finally conclude that:

- Divalent salts in the form of CaCl₂ or MgCl₂ have a negligible effect on the contact angle.
- N₂ is completely non-wetting of the surface and so N₂/water/quartz have a zero contact angle.
- H₂S is more absorbing on the quartz surface than CO₂. This means H₂S/water/quartz contact angles are larger than the corresponding CO₂/water/quartz under similar conditions of temperature and pressure.
- We have developed a consistent hydroxylated α -quartz model to measure CO₂/water/mineral contact angles that match experimental measurements to a larger extent than the fully coordinated α -quartz surface taken from Iglauer et al 2012.

We recommend that:

- The hydroxylated α -quartz surface should be made larger and run at more pressures and temperatures to see how contact angle varies.
- The pH is varied by removing hydrogen from the Silanols groups to form Si-O⁻ and see the effect on the contact angle.
- H₂S is simulated with this hydroxylated α -quartz surface to investigate if the contact angle is close to the values from experiment.

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Nomenclature

CCS	Carbon Capture and Storage
CO ₂	Carbon dioxide
H ₂ O	Water
M	Molarity
K	Degree Kelvin
θ	Contact Angle
γ	Interfacial Tension
Kg	Kilogram
m ³	Cubic Metre
nm	Nano Meter
Å	Armstrong
ε	Depth of Potential Well
σ	Distance at which the interparticle potential is zero
kJ	Kilo Joule
Mol	Moles
NaCl	Sodium Chloride
Na	Sodium
Cl	Chlorine
CaCl ₂	Calcium Chloride
MgCl ₂	Magnesium Chlorine
H ₂ S	Hydrogen Sulfide
N ₂	Nitrogen

Appendix A Critical Literature Review

MILESTONES IN “Molecular Dynamics Simulation of CO₂-fluid and CO₂-mineral interfacial properties: Application to subsurface gas injection (CCS projects)”

Year	Title	Authors	Contribution
1959	“Studies in Molecular Dynamics. I. General Method”	Alder, B. J. and Wainwright, T. E.	Introduced the concept of Molecular Dynamics by outlining overall method and approach as well as potential applications for the method.
1964	“Correlations in the Motion of Atoms in Liquid Argon”	Rahman, A.	Justification of the use of the molecular dynamic method with theoretical calculation matching the experimental data
1985	“Computer simulation of defect motion in model normal and ‘fast-ion’ conductors I. NaCl and AgCl”	Moscinski, J. and Jacobs, P. W. M.	Displayed the effective use of the individual ion displacements plots as well as the projection plots of the ions in the crystal lattice
1993	“The Potential for Aquifer disposal of carbon dioxide in the UK”	Holloway, S. and Savage, D.	Significant as an early proposal of carbon dioxide capture and disposal in UK and one of the first publications to discuss the various factors involved in the process in detail.
1994	“Aquifer Disposal of CO ₂ : Hydrodynamic and Mineral Trapping”	Bachu, S., Gunter, W. D. and Perkins, E. H.	An early effective overview of a geosequestration project, looking at Alberta Sedimentary Basin, from geological, core data as well as carbon capture/injection technology.
2006	“Wetting Phenomena at the CO ₂ /Water/Glass Interface”	Dickson, J. L., Gupta G., Horozov, T. S., Binks, B. P. and Johnston, K. P.	Demonstrated hysteresis of the advancing and receding contact angle with respect to pressurization and depressurization respectively with CO ₂ /water/ SiOH surface. Hysteresis was not observed on this surface however if repressurization was after 1 week exposure to CO ₂ .
2008	“Wettability Determination of the Reservoir Brine-Reservoir Rock System with Dissolution of CO ₂ at High Pressure and Elevated Temperatures”	Yang, D., Gu, G. and Tontiwachwuthikul, P.	Showed that intermediate –wet reservoir rock (determined by USBM/Amott analysis) could have CO ₂ /water/rock contact angles approaching and succeeding 90° implying CO ₂ partial wetting of the rock
2010	“Molecular dynamics simulation of wetting behaviour at CO ₂ /water/solid interfaces”	Liu, S. Y., Yang, X. N. and Qin, Y.	Used molecular dynamics simulation to model CO ₂ /water/solid interfaces and from this measure the contact angles in these simulations on hydrophilic and hydrophobic surfaces
2010	“Water-CO ₂ -mineral systems: Interfacial tension, contact angle and diffusion- Implications to CO ₂ geological storage”	D. Nicolas Espinoza and J. Carlos Santamarina	Performed interfacial property measurements on a wider range of surfaces that had been previously investigated. Also more effectively recreated pore fluid conditions to understand interfacial properties in actual CCS projects.
2011	“Residual CO ₂ imaged with X-ray micro-tomography”	Iglauer, S., Paluszny, A., Pentland, C. H., Blunt, M. J.	Confirmed that capillary pressure trapping of super-critical CO ₂ is locally a viable Carbon capture storage mechanism in clean sandstones
2011	“Residual Trapping in Simultaneous Injection of CO ₂ and Brine in Saline Aquifers”	Javaheri, M. and Jessen K.	Showed with four various aquifer settings that storage capacity varied significantly.
2011	“Measurements of capillary trapping of super-critical carbon dioxide in Berea sandstone”	Pentland, C. H., El-Maghraby, R. and Blunt, M. J.	Measured directly the amount of capillary trapping for the full range of initial saturation, known as the trapping curve, and the primary drainage capillary pressure on a Berea sandstone core (believe to be very much reprehensive of aquifer rocks)
2011	“Contact angle measurements of CO ₂ -H ₂ O-quartz/calcite systems in perspective of carbon sequestration”	Prem Kumar Bikkina	Measurement of contact angles of CO ₂ -H ₂ O on quartz and calcite surfaces. Experimentally looked at the influence of drop volume, pressure, temperature and repeated exposure of dense water saturated CO ₂ on contact angle.
2012	“Dewetting of Silica Surfaces upon Reaction with Supercritical CO ₂ and Brine: Pore-Scale Studies in Micromodels”	Kim, Y., Wan, J., Kneafsey, T. J. and Tokunaga, T. K.	Purposed with results from their experiments, and others in the literature, mechanisms responsible for dewetting of silica surface and changes to chemical structure of silica surface that cause the observed characteristics (such as why pressure increase increases contact angle)
2012	“Predicting CO ₂ -water interfacial tension under pressure and temperature conditions of geologic CO ₂ storage”	Nielsen et al.	Performed Molecular dynamics simulation and compared simulation results to experimental from using different force field parameters and molecular models

SPE 144613 (2011)

Residual Trapping in Simultaneous Injection of CO₂ and Brine in Saline Aquifers

Authors: Javaheri, M. et al

Contribution

Showed with four various aquifer settings that aquifers storage capacity varied significantly. Also demonstrated that CO₂ trapping fraction is increased in residual phase with higher injection rate of brine. Lastly displayed reduction of relative permeability (both phases) majorly impacts the sweep efficiency of the injected CO₂ and so with affect the level of residual entrapment as well as the distance travelled before full segregation.

Objectives:

To use computer simulation to model residual trapping of Carbon dioxide in various aquifer settings.

Methodology:

Used Computer Simulations with CMG-GEM (2009), a commercial compositional reservoir simulator and performed simulations on 2D grid block domain (4000mx200m). They addressed the role of residual entrapment of CO₂ in the content of dimensionless groups introduced by Zhou et al. (1994).

Conclusions:

1. Brine injection slows down the vertical migration of CO₂ by decreasing the gravity number, making the gravity force less significant relative to viscous force.
2. The storage capacity is significantly influenced by aquifer setting with cold aquifers having a larger storage capacity compared to warm ones.
3. Though final fraction of injected CO₂ may be the same between aquifers, the transient behaviour is very different. By including a counter-current relative permeability model into the simulation the estimate of CO₂ trapped increases significantly.

Comments:

Insightful paper to understanding how Carbon storage can be simulated as well as looking at the properties that overall effect carbon storage on a reservoir level with respect to temperature and depth of reservoir as well as heterogeneity with respect to permeability. I believe however hydrodynamic trapping was used in the wrong context in the introduction and the author confused the term with what it should be known as structural trapping.

J. Chem. Phys. 31, 459 (1959); doi: 10.1063/1.1730376

Studies in Molecular Dynamics. I. General Method

Authors:

Alder, B. J. and Wainwright, T.E

Contribution:

Introduced the concept of Molecular Dynamics by outlining overall method and approach as well as potential applications for the method.

Objectives:

To clearly outline the method and how computers can be used to numerically solve the classical equations of motion once the force field is calculated.

Methodology:

Use of classical physics to understand the many body problem that is presented when calculating the behaviour of several hundred interacting classical particles.

Conclusions:

1. Limitations of the method include the size of system due to memory capacity, speed of the computing machines, difficulty with slow convergence and capturing long-range potentials accurately between particles.
2. The method involves setting the initial positions of the particles and computing the forces between the particles. With this force calculated and selection of a time step the particles are moved then once at the new position the forces are recalculated and then moved again for the duration the time step. This process is repeated until necessary.

Comments:

Fundamental to the concept of molecular dynamics being introduced into the general literature.

Phys. Rev. 136, A405–A411 (1964)
Correlations in the Motion of Atoms in Liquid Argon

Authors:

Rahman, A

Contribution:

Investigation into a classical 864-body problem with a truncated two-body interaction of the Lennard-Jones type, with periodic boundary conditions. This paper further justified the use of the molecular dynamic method with theoretical calculation matching the experimental data. Also developed algorithms used in molecular dynamics simulations, some which are still used today.

Objectives:

To study liquid argon with molecular dynamics and compare how accurate the predictions would be compared to experimental results.

Methodology:

Molecular dynamic study for liquid argon using the CDC 3600 digital computer.

Conclusions:

1. Value of the diffusion constant obtained was in good agreement with the observed value meaning the time-dependent mean-square displacement obtained is likely to be correct. The pair-distribution function was in good agreement with the observed one.
2. The variation in the diffusion constant with temperature and density was also in fairly good agreement with the variation measured in the laboratory (Naghizadeh and Rice (1962)).

Comments:

In scientific circles Rahman is commonly known as the father of molecular dynamics. This publication proved the method validity and opened up the wide range of possible applications the method can have with the correct amount of computational power and correct assumptions

Fuel 89 (2010) 2651-2664

A review of studies on CO₂ sequestration and caprock integrity

Authors:

Shukla, R. et al

Contribution:

None but an up-to-date (2010) review on CO₂ sequestration and caprock integrity. The paper provides an overview of CCS research around the world looking at the geosequestration system and the different trapping mechanisms (having a large focus on caprock integrity)

Objectives:

To outline clearly the subject of CO₂ sequestration and caprock integrity and review the various problems associated with the subject.

Methodology:

Review all the major papers published with respect to Carbon Capture and sequestration (CCS)

Conclusions:

1. Past and current geosequestration projects suggests it is feasible to store CO₂ in subsurface formations.
2. Geomechanical and geochemical properties of the reservoir and caprock have a great influence in the outcome of the project. The chemical interaction of the carbon dioxide with the rock minerals and groundwater should be studied with special consideration of the effects of other processes on the path and reaction rate.
3. Different effects if natural and human activities should be investigated to understand the long-term safety of sequestration projects.

Comments:

This is a very good overall review of CCS which had a very interesting focus on caprock integrity. Most of the review is not completely applicable to this project as looking at the mechanism of residual trapping as well as, with respect to structural trapping, the effective use of capillary trapping in cap rock.

Energy Convers. Mgmt Vol. 35, No. 4, pp. 269-279 (1994)
 Aquifer Disposal of CO₂: Hydrodynamic and Mineral Trapping

Authors:

Bachu, S. et al

Contribution:

An early effective overview of a geosequestration project, looking at Alberta Sedimentary Basin, from geological, core data as well as carbon capture/injection technology.

Objectives:

To purpose the problems, potential solutions and generally discuss aquifer disposal of CO₂ using the Alberta Sedimentary Basin as a case study

Methodology:

Analysis of data from the Alberta Sedimentary Basin (Western Canada) and investigation into its potential use in a geosequestration project specifically analysing hydrodynamic trapping, mineral trapping and CO₂-storage capacity of the basin with information from literature

Conclusions:

1. The Alberta Basin has several deep aquifers for which there is enough data to estimate regional scale CO₂ disposal potential.
2. Chemistry of formation water and rock mineralogy may increase or decrease the potential for CO₂ capture through geochemical reactions (mineral trapping). Dissolved and immiscible CO₂ will travel with the velocity of the formation water and so for large sedimentary basins, like the Alberta Basin, this leads to hydrodynamic trapping of CO₂.
3. Hydrodynamic trapping enhances potential for mineral trapping and thus there is a need for stratigraphic traps or depleted hydrocarbon reservoirs in the vicinity of CO₂-emitting power plants.

Comments:

A very early paper published that discussed Aquifer Disposal of CO₂ as a viable scheme. Give early insight to the mechanism of carbon dioxide trapping in aquifers.

GEOPHYSICAL RESEARCH LETTERS, VOL. 38, L21403 (2011)

Residual CO₂ imaged with X-ray micro-tomography

Authors:

Iglauer, S. et al

Contribution:

Confirmed that capillary pressure trapping of super-critical CO₂ is locally a viable Carbon capture storage mechanism in clean sandstones

Objectives:

To produce images of CO₂ trapped in pore with X-ray micro-tomography to investigate/confirm if capillary pressure trapping was a viable mechanism to stop CO₂ escaping from reservoir rock.

Methodology:

Used a novel high-pressure elevated-temperature micro-flow cell to image trapped clusters of super-critical CO₂ at the pore scale

Conclusions:

1. CO₂ can be trapped by capillary action.
2. There is a low super-critical CO₂ residual saturation for a strongly water-wet system with fewer small clusters, however the clusters are of all sizes, up to the system size, providing a large surface area for dissolution and reaction leading, again, to reduced CO₂ leakage risk.

Comments:

Outlined technique to image CO₂ trapping on a pore scale and this may be a used technique in future analysis of proposed CCS projects

International Journal of Heat and Mass Transfer 45 (2002) 3771-3780

Contact angles and interface behaviour during evaporation of liquid on a heated surface

Authors:

Kandlikar, S.G. and Steinke, M.E.

Contribution:

None significant to area of project

Objectives:

To outline a historical review of the available literature on the photographic studies in pool and flow boiling

Methodology:

Review paper of all the major papers published with respect to Contact angles and interface behaviour during evaporation of liquid on a heated surface

Conclusions:

1. Contact angles are dependent on the surface roughness.
2. It is observed that on very smooth surfaces, the contact angle is seen to be higher and that as surface roughness is increased the contact angles first decrease however then start increasing with increasing surface roughness.

Comments:

Interesting to see a review on measurements and modelling of contact angles/interface behaviour in a completely different area to this project.

Chinese Science Bulletin Vol.55 No.21 2252-2257 (2010)

Molecular dynamics simulation of wetting behaviour at CO₂/water/solid interfaces

Authors:

Liu, S.Y, et al.

Contribution:

Understanding scCO₂ cleaning properties with respect to the preparation of semiconductor devices. With respect to this project it displayed that molecular simulation could repeat experimental results with respect to CO₂/water/quartz interfaces

Objectives:

To successfully model CO₂/water/solid interfaces and match the simulation results with experimental results

Methodology:

Used molecular dynamics simulation to model CO₂/water/solid interfaces and from this measure the contact angles in these simulations on hydrophilic and hydrophobic surfaces.

Conclusions:

1. In the hydrophobic surface the water droplet loses contact with the surface (increasing contact angle at first) with the addition of CO₂ fluid.
2. The hydrophilic surface contact angle of the water droplet on the surface increases with increasing CO₂ density suggesting the CO₂ environment modifies the surface wetting properties.
3. The molecular simulation gives a result consistent with the previous experimental reports.

Comments:

The surface may not be truly represented in these simulations hence it may not be suitable to use the surfaces used here in our simulations. Note reference to methods that was used to evaluate contact angles from simulation. Effectively what this project (and related with-in the same group) is to the geoen지니어ing industry, is this paper to the semiconductor industry.

Environ. Sci. Technol. 46, 4228-4235 (2012)

Dewetting of Silica Surfaces upon Reaction with Supercritical CO₂ and Brine: Pore-Scale Studies in Micromodels

Authors:

Kim, Y et al.

Contribution:

Purposed with results from their experiments, and others in the literature, mechanisms responsible for dewetting of silica surface and changes to chemical structure of silica surface that cause the observed characteristics (such as why pressure increase increases contact angle).

Objectives:

To understand if, and to what extent, interaction with supercritical carbon dioxide change the wettability of silica (a common reservoir sold).

Methodology:

Use of High pressure microscopy to observe with-in a micromodel system (which is fused silica plates etched with hydrofluoric acid) with brine and CO₂ present the contact angles under varying conditions.

Conclusions:

1. Carbon Dioxide cannot be treated as a simple nonwetting fluid in reservoir pores and that supercritical CO₂ can react quickly (within seconds) with silica resulting in dewetting of the silica surface. The contact angle increased with increasing ionic strength however we do not yet know if the dewetting phenomenon observed on silica also occurs on other mineral surfaces.

Comments:

Key paper in understanding what the surface of the crystal quartz may be after CO₂ injection and how this may affect wettability of rock over time.

Proc. R. Soc. Lond. A 398, 141-171 (1985)

Computer simulation of defect motion in model normal and 'fast-ion' conductors I. NaCl and AgCl

Authors:

Moscinski, J and Jacobs, P. W. M

Contribution:

Significant in understanding better the use of analysing partial radial distribution functions, mean square displacements and the velocity autocorrelation function. The paper also displayed the effective use of the individual ion displacements plots as well as the projection plots of the ions in the crystal lattice.

Objectives:

To use molecular dynamics to study defects in crystals and the mechanisms taking place with-in the lattice that could not, to me knowledge at the time, be observed by experiment.

Methodology:

Molecular dynamics simulation technique was used to study Frenkel defects in crystalline NaCl and AgCl. Partial radial distribution functions, mean square displacements and the velocity autocorrelation function were calculated for anion and cation species.

Conclusions:

1. Collinear interstitial migration, vacancy jumps and direct interstitial jumps are the processes observed from molecular dynamics that allow the recombination of Frenkel defects in NaCl and AgCl crystals.
2. The other publication (Moscinski and Jacobs 1985) is a similar study but outline the use of SrCl₂ as a 'fast ion' conductor.

Comments:

In the paper there is a very good outline of the history in molecular dynamics as well as more detail on the molecular dynamic simulation method and details of the calculations. Generally considered a very important 'recent' paper with respect to molecular dynamics.

Energy Convers. Mgmt Vol. 34, No. 9-11, pp. 925-932 (1993)
The Potential for Aquifer disposal of carbon dioxide in the UK

Authors:

Holloway, S and Savage, D

Contribution:

Significant as an early proposal of carbon dioxide capture and disposal in UK and one of the first publications to discuss the various factors involved in the process in detail.

Objectives:

To investigate the concept of carbon dioxide disposal with using the UK as a case study.

Methodology:

General discussion about carbon dioxide storage in the UK through analysis of geological information, petrophysical considerations, geochemistry and practical implications.

Conclusions:

1. The CO₂ produced from power plants in the UK (1993 level) are too large to be practically stored in the UK's oil and gas reservoirs.
2. Onshore underground disposal of CO₂ would probably be the most practical with these good quality reservoir rocks combined with large closures are still to be found with-in the UK (1993).

Comments:

Referred to a paper not published as from a British Coal Organisation. Another early paper to practically discuss CCS projects so much so that it was referred to as Carbon dioxide disposal.

GEOPHYSICAL RESEARCH LETTERS, VOL. 38, L06401, (2011)

Measurements of capillary trapping of super-critical carbon dioxide in Berea sandstone

Authors:

Pentland, C.H. et al.

Contribution:

Measured directly the amount of capillary trapping for the full range of initial saturation, known as the trapping curve, and the primary drainage capillary pressure on a Berea sandstone core (believe to be very much representative of aquifer rocks)

Objectives:

To perform measurements of capillary trapping on a real reservoir rock consider to be a good representation of man reservoir rocks.

Methodology:

Used the semi-permeable disk (porous-plate) coreflood method to experimentally measure drainage capillary pressure and the relationship between initial and residual non-wetting phase saturation for a supercritical carbon dioxide brine system.

Conclusions:

1. Experimentally there is evidence of CO₂ being trapped by capillary forces after the re-injection of brine.
2. The dimensionless capillary pressure (J-Function) for the oil-brine system is similar to the CO₂-brine system.
3. Discrepancy at low pressure (corresponding to low non-wetting phase saturations) could be caused by dynamic effects, pressure fluctuations or subtle differences in wettability.

Comments:

Similar to experiments and measurements carried out by Dr Iglauer's group.

Energy & Fuels, 22, 504-509 (2008)

Wettability Determination of the Reservoir Brine-Reservoir Rock System with Dissolution of CO₂ at High Pressure and Elevated Temperatures

Authors:

Yang, D. et al.

Contribution:

Outlined an effective experimental method to determine the wettability of the reservoir brine-reservoir rock system with the ADSA technique for the sessile drop case. The paper also showed that intermediate –wet reservoir rock (determined by USBM/Amott analysis) could have CO₂/water/rock contact angles approaching and succeeding 90° implying CO₂ partial wetting of the rock.

Objectives:

To outline an experimental technique to determine the wettability of CO₂-reservoir brine-reservoir rock as high pressures and temperatures using the ADSA technique.

Methodology:

Used the ADSA (axisymmetric drop shape analysis) technique to experimentally determine the wettability of a reservoir brine reservoir rock system.

Conclusions:

1. The reservoir brine sample (collected from the Weybirn oil field, Canada) had an increasing contact angle with increasing pressure and a decreasing contact angle with increasing temperature. This is attributed to higher CO₂ solubility at higher pressure but lower CO₂ solubility at higher temperature.
2. Another increasing conclusion was higher pressure changed the reservoir rock from hydrophilic to hydrophobic allowing more ease to displace brine from injecting CO₂ therefore increasing CO₂ storage capacity.

Comments:

ASDA technique is considered very accurate with respect to contact angle measurement as well as being fully automatic and completely free of the operator's subjectivity. Significant implication of potential CO₂ wet rock as this would mean the CO₂ relative permeability would not reach 0 therefore meaning CO₂ would not be trapped by capillary trapping.

Lagmuir 22, 2161-2170 (2006)

Wetting Phenomena at the CO₂/Water/Glass Interface

Authors:

Dickson, J. L. et al.

Contribution:

Demonstrated hysteresis of the advancing and receding contact angle with respect to pressurization and depressurization respectfully with CO₂/water/ 37% SiOH surface. Hysteresis was not observed on this surface however if re pressurization was after 1 week exposure to CO₂.

Objectives:

To measure CO₂/water/solid contact angle values on two glass substrates with different hydrophilicities versus pressure in a novel apparatus and to understand how long/short range interactions with the silanol groups influence the relevant interfacial energies and contact angle.

Methodology:

Experimental apparatus set-up (see paper) to carry out high-pressure contact-angle measurements of the CO₂/water/solid interface (the solid interface in these experiments being glass microscope slides).

Conclusions:

1. Contact angles increased significantly as the CO₂ pressure increased from atmospheric to vapour pressure.
2. The greater degree of hysteresis for the less hydrophobic silica can be attributed in part to the capping of silanol groups with CO₂.
3. The model used to address long-range forces was accurate for predicting the contact angle with a small silanol concentration of 12% but under-predicted it for the 37% SiOH surface.
4. CO₂ is more effective than many organic solvent in removing water from silica even when water is more soluble in the organic solvent.

Comments:

Hysteresis not being observed on the silica surface if re pressurization was after 1 week exposure to CO₂ suggests that hysteresis was due to contact angle not reaching equilibrium before measurement.

Geochimica et Cosmochimica Acta 81 (2012) 28–38

Predicting CO₂-water interfacial tension under pressure and temperature conditions of geologic CO₂ storage

Authors:

Nielsen et al.

Contribution:

With molecular dynamics simulations successfully modelled interfacial tension variation in a CO₂-water-mineral surface over various pressures and temperatures conditions that relate to CCS projects

Objectives:

To use molecular simulation to enhance the utility of limited data when used to validate assumptions made in interpretation, resolve discrepancies among the data and fill gaps where data are lacking.

Methodology:

Performed Molecular dynamics simulation, compared simulation results from using different force field models and compared these simulations to experimental results (not as extensive)

Conclusions:

1. In range of temperature and pressure relevant to CO₂ sequestration the PPL CO₂-water interaction gives the most accurate CO₂ surface excess and pressure dependence on interfacial tension.
2. PPL-SPC/E simulation when renormalized to TIP4P2005 water's surface tension reproduce experimental interfacial tension measurements
3. PPL-TIP4P2005 simulations reproduce both experimental water surface and interfacial tension extremely well without any need of renormalization.
4. The PPL-SPC/E model has more tested interaction potentials available for use and so may be better than PPL-TIP4P2005 model to study related CCS problems.

Comments:

Up-to-date work on modelling interfacial tension similar this project and useful to review how effective the various force fields were at recreating experimental observations in the literature.

Journal of Colloid and Interface Science (2012) JCIS 18002

Molecular dynamics computations of brine-CO₂ interfacial tensions and brine-CO₂-quartz contact angles and their effects on structural and residual trapping mechanisms in carbon geo-sequestration

Authors:

S. Iglauer, M.S. Mathew and F. Bresme

Contribution:

With molecular dynamics simulation matched of experimental interfacial tension data with simulation data. Also suggested that simulations on a fully co-ordinated silica surface is not representative of the many experimental conditions used in previous contact angle measurements.

Objectives:

Similar to that of Nielsen et al. expect this time investigating more factors, such as salinity, and now measuring how contact angle varies.

Methodology:

Performed Molecular dynamics simulation firstly validating it's use then performing simulations over a wide range conditions to compare to experiment and understand effects such as pressure, temperature and salinity.

Conclusions:

1. θ strongly increases with increasing pressure until approximately the saturation pressure of CO₂ is reached. Above the saturation pressure, θ increases slightly with further pressure increase. This is consistent with Chiquet et al.'s measurements.
2. θ decreases with temperature in the interval 0-17 MPa, consistent with experimental data.
3. Simulations found no evidence for a systematic increase or decrease of the contact angle with salt concentration.
4. MD results imply that lower pressures and higher temperatures are favourable storage conditions, while high salt concentrations can be tolerated as salinity has only a marginal influence.

Comments:

Fundamental work in which this project is simply a continuation of this work looking at construct a hydroxylated silica surface to explain differences in experimental contact angle measurements and to look how other gases and salts (divalent) may affect contact angle on the fully coordinated surface already constructed.

International Journal of Greenhouse Gas Control -414

Contact angle measurements of CO₂-water-quartz/calcite systems in the perspective of carbon sequestration.

Author:

Prem Kumar Bikkina

Contribution:

Investigated the influence of drop volume, pressure, temperature and repeated exposure of dense water saturated CO₂ on contact angle

Objectives:

To measure how contact angle varies with pressure, temperature, size of water drop and number of CO₂ exposure cycles.

Methodology:

Use of custom made, high pressure (10,000 psig) and high temperature (350 °F) sustainable, Goniometer to measure interfacial properties

Conclusions:

1. Repeated exposure to dense water saturated CO₂ brought forward a permanent shift in the contact angle. Such a permanent shift in the contact angle is remarkably distinct with the contact angle shifts associated with variation in pressure.
2. Better site characterization studies are recommended to instill confidence in the selection of design parameters associated to CO₂ sequestration sites.
3. Other contact angle data trends observed with temperature and pressure agreed with the trends available in the literature.

Comments:

Consistency of contact angle measurements with other in the literature suggest contact angles should be able to be successfully modelled if molecular surface is created.

WATER RESOURCES RESEARCH, VOL. 46, W07537 (2010)

Water-CO₂-mineral systems: Interfacial tension, contact angle and diffusion-Implications to CO₂ geological storage.

Authors:

D.Nicolas Espinoza and J.CarlosSantamarina

Contribution:

Performed interfacial property measurements on a wider range of surfaces that had been previously investigated. Also more effectively recreated pore fluid conditions to understand interfacial properties in actual CCS projects.

Objectives:

To extend scope of previous experimental studies measuring interfacial tension and the contact angle in application to further understand CCS projects

Methodology:

Used the sessile droplet method to determine the evolution in interfacial tension and the contact angle.

Conclusions:

1. Dissolved organic or inorganic species in water preferentially organize at the interface.
2. On hydrophobic substrates, the increase in contact angle _ with pressure can be as high as 60°. Oil wet mineral surfaces may turn from hydrophilic at low gas pressure to hydrophobic at high gas pressure.
3. Capillary pressure and viscous forces play an important role in determining CO₂ injectability and the sealing capacity of geological formations.
4. The breakthrough pressure is a function of sediment characteristics (primarily specific surface), overburden effective stress, and fluid pressure-dependent wetting conditions (interfacial tension and contact angle).

Comments:

Good extension of previous experimental work on measuring interfacial properties that affect CCS projects

Appendix B A selection of C Programs wrote by the author to help with editing files that go into the simulation**Program 1**

```
//A program to take CO2 molecules and replace them with H2S molecules//
#include <stdio.h>
#include <stdlib.h>

int main ( int argc, char * argv[] )

{
//declaration of GLOBAL variable i and will number each round of printing
CONFIG data//
  int i;

for(i=31059; i < 32531;i = i + 3)
{
  double a, b, c, d, e, f, g, h, j, k, p, q, r, s, t, u, v, w, x, y, ab, ac,
ad, ae, af, ag, ah, ai, aj, ak;
  char l, m, n, z, aa, al, o, am;

//declaration of variable within for loop hoping to get each component of the
CONFIG file//

scanf("%c%c          %lf\n", &l, &m, &a);
scanf(" %lf      %lf      %lf\n", &b, &c, &d);
scanf(" %lf      %lf      %lf\n", &e, &f, &g);
scanf(" %lf      %lf      %lf\n", &h, &j, &k);

scanf("%c%c%c          %lf\n", &n, &o, &al, &p);
scanf(" %lf      %lf      %lf\n", &q, &r, &s);
scanf(" %lf      %lf      %lf\n", &t, &u, &v);
scanf(" %lf      %lf      %lf\n", &w, &x, &y);

scanf("%c%c%c          %lf\n", &z, &aa, &am, &ab);
scanf(" %lf      %lf      %lf\n", &ac, &ad, &ae);
scanf(" %lf      %lf      %lf\n", &af, &ag, &ah);
scanf(" %lf      %lf      %lf\n", &ai, &aj, &ak);

//defined in the middle of loop that printing and scanning config file as a
trio of parts//
  int xy, xz;
  xy=i+1;
  xz=i+2;

//now printing the components of the CONFIG file again but this time with the
right atomic index//

printf("S          %d\n", i);
printf("      %lf          %lf          %lf\n", b, c, d);
printf("      %lf          %lf          %lf\n", e, f, g);
printf("      %lf          %lf          %lf\n", h, j, k);
```

```
//will now define new positions of H2S but S simply replaces where C was on
CO2 previously//
```

```
double ao, ap, aq, as;

ao=b+0.97752;    //defining new x position of H2S//
ap=b-0.97752;

if(i%2==0)
{
aq=c-0.952484;
as=c-0.952484;
}
else
{
aq=c+0.952484;
as=c+0.952484;
}

printf("H2S          %d\n", xy);
printf("          %lf          %lf          %lf\n", ao, aq, d);
printf("          %lf          %lf          %lf\n", t, u, v);
printf("          %lf          %lf          %lf\n", w, x, y);

printf("H2S          %d\n", xz);
printf("          %lf          %lf          %lf\n", ap, as, d);
printf("          %lf          %lf          %lf\n", af, ag, ah);
printf("          %lf          %lf          %lf\n", ai, aj, ak);
}

return 0;
}
```

Program 2

```
//program to insert N2 molecules in on CO2 molecules//
#include <stdio.h>
#include <stdlib.h>

int main ( int argc, char * argv[] )

{
    int i;

//scan CO2 molecules by scanning 3 atoms at a time// with the loop i <
(number of CO2 molecules + 1) in this case there were 1094//
    for(i=1; i < 1095; i++)
    {
        int j;
        char a, b, c;
        scanf("%c%c%c      %d\n", &a, &b, &c, &j);

        double xp, yp, zp;
        scanf("%lf %lf %lf\n", &xp, &yp, &zp);
```

```

int ja;
char aa, ba, ca;
scanf("%c%c%c %d\n", &aa, &ba, &ca, &ja);

double xpa, ypa, zpa;
scanf("%lf %lf %lf\n", &xpa, &ypa, &zpa);

int jb;
char ab, bb, cb;
scanf("%c%c%c %d\n", &ab, &bb, &cb, &jb);

double xpb, ypb, zpb;
scanf("%lf %lf %lf\n", &xpb, &ypb, &zpb);

//replaces C with N//
printf("N %d\n %lf %lf %lf\n", j,
xp, yp, zp);
int jc;
jc=j+1;
double xpnew, ypnew, zpnew;
xpnew=xp;
zpnew=zp;
ypnew=yp+1.09986;
printf("N %d\n %lf %lf %lf\n", jc,
xpnew, ypnew, zpnew);
// and printit second N it's bond length away in the y axis //
}

return 0;
}

```

Program 3

```

//very simple, but very useful, program to renumber separate CONFIG files put
together and are not numbered correctly//
#include <stdio.h>
#include <stdlib.h>

int main ( int argc, char * argv[] )

{
int i;

//loop set up to renumber the CONFIG data// i < (number of atoms +1)// in
this case there are 41067 atoms in total to be renumbered//
for(i=1; i < 41068; i++)
{
int j;
char a, b, c;
scanf("%c%c%c %d\n", &a, &b, &c, &j);

//scans the position, velocity and acceleration in the x,y and z directions//
double xp, yp, zp;

```

```

scanf("%lf %lf %lf\n", &xp, &yp, &zp);
double xv, yv, zv;
scanf("%lf %lf %lf\n", &xv, &yv, &zv);
double xa, ya, za;
scanf("%lf %lf %lf\n", &xa, &ya, &za);

//prints only the x,y z positions that were scanned//
printf("%c%c%c      %d\n      %lf      %lf      %lf\n",
a, b, c, i, xp, yp, zp);
}

return 0;
}

```

Program 4

```

//Program to clean excess CO2 molecules in CONFIG file//
#include <stdio.h>
#include <stdlib.h>

int main ( int argc, char * argv[] )

{
    int i;

//loop declared to scan 3 atoms a time which are the C and two OC2//
// i < (number of CO2 molecules + 1)// in this example case there were 16193
CO2 molecules to scan//

for(i=1; i < 16194; i++)
{
    int ja;
    char aa, ba, ca;
    scanf("%c%c%c      %d\n", &aa, &ba, &ca, &ja);

    double xpa, ypa, zpa;
    scanf("%lf %lf %lf\n", &xpa, &ypa, &zpa);

    int jb;
    char ab, bb, cb;
    scanf("%c%c%c      %d\n", &ab, &bb, &cb, &jb);

    double xpb, ypb, zpb;
    scanf("%lf %lf %lf\n", &xpb, &ypb, &zpb);

    int jc;
    char ac, bc, cc;
    scanf("%c%c%c      %d\n", &ac, &bc, &cc, &jc);

    double xpc, ypc, zpc;
    scanf("%lf %lf %lf\n", &xpc, &ypc, &zpc);

    double zlowerlimit, zhigherlimit;

```



```

    zlowerlimit=6.0;
    zhigherlimit=69.0;
//limits of where the CO2 want to be kept//
//the if else statements are used to ensure if an part of the CO2 molecule is
outside the limits in the z axis they will be deleted by not being printed//

    if(zpa<zlowerlimit)
    {

    }
    else if(zpb<zlowerlimit)
    {
    }
    else if(zpc<zlowerlimit)
    {
    }
    else if(zpa>zhigherlimit)
    {

    }
    else if(zpb>zhigherlimit)
    {
    }
    else if(zpc>zhigherlimit)
    {
    }
    else
    {
//here printing the CO2 molecules that are with in the limits//
    printf("%c%c%c          %d\n      %lf          %lf\n",
aa, ba, ca, ja, xpa, ypa, zpa);
    printf("%c%c%c          %d\n      %lf          %lf\n",
ab, bb, cb, jb, xpb, ypb, zpb);
    printf("%c%c%c          %d\n      %lf          %lf\n",
ac, bc, cc, jc, xpc, ypc, zpc);
    }

    }

return 0;
}

```

Program 5

```

//part of the program to cut the frozen fully coordinated at certain points
and cap it with Hydroxyl groups to form silanols//
#include <stdio.h>
#include <stdlib.h>
#include <math.h>

int main ( int argc, char * argv[] )

{
    int i;

```

```

//loop to scan the 17280 atoms in the frozen quartz crystal//
for(i=1; i < 17281; i++)
{
int j;
char a, b;
scanf("%c%c %d\n", &a, &b, &j);
double xp, yp, zp;
scanf("%lf %lf %lf\n", &xp, &yp, &zp);

        if(zp>3.5) //just to edit top surface of crystal//
        {
                double PIEreal, PIElarge;

                PIElarge=rand() % 628318;
                PIEreal=PIElarge/100000;
                //generates a random double number between 2 PIE and
O//

                                //mapped out coordinates from the
crystal to hydroxylate the surface non uniformly//
                                if(yp>-47 && yp<-44 && xp>-46 &&
xp<-32)
                                {
                                        double xpnew1, ypnew1, zpnew1,
xpnew2, ypnew2, zpnew2; //defines new positions of surface O-H groups//
                                        if(a=='S')
                                        {
                                                xpnew1=xp;
                                                ypnew1=yp;
                                                zpnew1=zp+1.61; //places O
atoms above dangling Si atoms//
                                                xpnew2=xpnew1+0.975*sin(1.003)*cos(PIEreal);
                                                ypnew2=ypnew1+0.975*sin(1.003)*sin(PIEreal);
                                                zpnew2=zpnew1+0.975*cos(1.003);

                                                //spherical to cartesian
coordinates equations used here//
                                                //prints the new atoms
with x after the Si and O to note that is where Hydroxylation is//
                                                printf("Six
%d\n %lf %lf %lf\n", i, xp, yp, zp);
                                                printf("Ox
%d\n %lf %lf %lf\n", i, xpnew1, ypnew1, zpnew1);
                                                printf("H
%d\n %lf %lf %lf\n", i, xpnew2, ypnew2, zpnew2);
                                                }
                                                else if(zp>5)
                                                {
                                                        //deleted bridging oxygen
atom//
                                                }
                                                else

```

```

affected//
                                                                    {
                                                                    //prints rest of atoms not
                                                                    printf("%c%c
%d\n    %lf          %lf          %lf\n", a, b, i, xp, yp, zp);
                                                                    }
                                                                    }
                                                                    //mapped out coordinates from the
crystal to hydroxylate the surface non uniformly//
                                                                    else if(yp>-34 && yp<-32 && xp>-34
&& xp<-15)
                                                                    {
                                                                    double xpnew1, ypnew1, zpnew1,
xpnew2, ypnew2, zpnew2; //defines new positions of surface O-H groups//
                                                                    if(a=='S')
                                                                    {
                                                                    xpnew1=xp;
                                                                    ypnew1=yp;
                                                                    zpnew1=zp+1.61;

xpnew2=xpnew1+0.975*sin(1.003)*cos(PIEreal);
ypnew2=ypnew1+0.975*sin(1.003)*sin(PIEreal);
zpnew2=zpnew1+0.975*cos(1.003);

                                                                    printf("Six
%d\n    %lf          %lf          %lf\n", i, xp, yp, zp);
                                                                    printf("Ox
%d\n    %lf          %lf          %lf\n", i, xpnew1, ypnew1, zpnew1);
                                                                    printf("H
%d\n    %lf          %lf          %lf\n", i, xpnew2, ypnew2, zpnew2);
                                                                    }
                                                                    else if(zp>5)
                                                                    {
                                                                    }
                                                                    else
                                                                    {
                                                                    printf("%c%c
%d\n    %lf          %lf          %lf\n", a, b, i, xp, yp, zp);
                                                                    }
                                                                    }
                                                                    //may more else if statement in real
program but very long file so just showing general idea of program//
                                                                    else
                                                                    {
                                                                    printf("%c%c          %d\n
%lf          %lf          %lf\n", a, b, i, xp, yp, zp);
                                                                    }
                                                                    }
                                                                    else
                                                                    {
                                                                    printf("%c%c          %d\n    %lf          %lf
%lf\n", a, b, i, xp, yp, zp);
                                                                    }
                                                                    }
                                                                    //last else statements to print other atoms not affected//

```

```

    }
return 0;
}

```

Program 6

```

//program to print large part of FIELD file from newly created CONFIG file//
#include <stdio.h>
#include <stdlib.h>

int main ( int argc, char * argv[] )

{

    int i;

//loop to scan the CONFIG file with i < (number of atoms scanned +1)//
for(i=1; i<17836; i++)
{
    int j;
    char m, n, l;
    double x, y, z;
    scanf("%c%c%c %d\n %lf %lf %lf\n", &m, &n, &l, &j, &x, &y, &z);

        if(m=='S')
        {

                printf("%c%c%c          28.0855          2.400          1
1\n", m, n, l);

        }
        else if(m=='O')
        {

                printf("%c%c%c          16.0000          -1.200          1          1\n",
m, n, l);

        }
        else
        {
                printf("%c%c%c          1.0080          0.600          1          1\n", m, n,
l);
        }
//prints the mass, charge, repeat unit and 1 as to freeze the atoms in
place//
    }

return 0;
}

```

Appendix C Overview of Results obtained

Simulations from Divalent Salts

Pressure (Mpa)	Error (Mpa)	Temperature	Salt	Concentration (M)	Angle	Error
1.7	0.4	300	CaCl ₂	1	62.2	3.5
11.6	0.4	300	CaCl ₂	1	81.3	0.3
14.2	1.5	300	CaCl ₂	1	81.2	0.5
1.6	0.3	300	MgCl ₂	1	59.2	2.3
1.4	0.4	300	MgCl ₂	4	65.5	1.9
1.6	0.4	300	CaCl ₂	4	69.0	2.1

Simulations from H₂S

Conditions	Pressure (Mpa)	error (Mpa)	Temperature	Angle	Error
50% H ₂ S 50% CO ₂	9.5	0.5	350	79.7	2.0
100% H ₂ S	19.4	0.9	350	78.3	2.1
100% H ₂ S	20.8	1.1	350	80.3	0.3
100% H ₂ S	6.0	0.0	350	79.8	1.6
100% H ₂ S	2.9	0.6	350	66.2	1.5

Simulations with Hydroxylated Surface

Surface Conc- of OH (OH/nm ²)	Pressure (Mpa)	error	Contact Angle (°)	error
4.5	10.2	0.3	34.7	1.7
3.7	10.2	0.3	36.0	0.9
1.7	10.3	0.8	43.4	1.8
1.7	12.7	0.4	50.0	2.0

Simulation from N₂

Pressure (Mpa)	error	Temperature (K)	Angle	error	Comments
10	0.4	300	0	N/A	Water wet surface
12	0.6	350	0	N/A	Water wet surface

Appendix D Snapshots

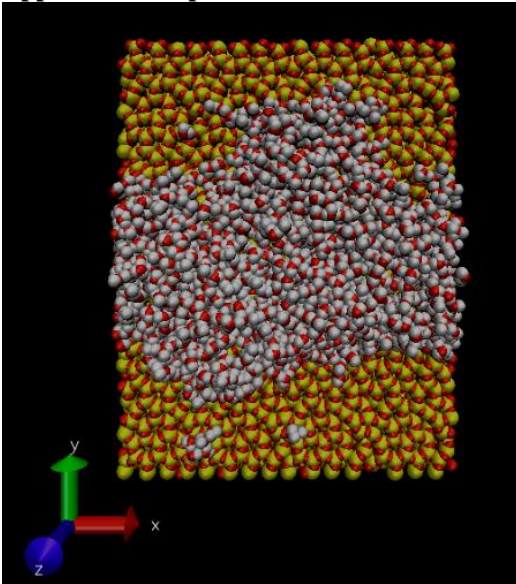


Figure showing water completely wetting the surface with simulation of N₂/water/quartz (N₂ removed for easier viewing).

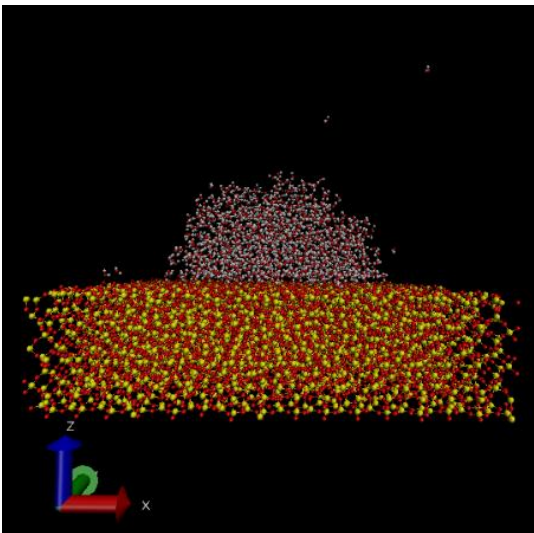


Figure showing droplet on fully coordinated surface after simulated with H₂S (H₂S removed for easier viewing)

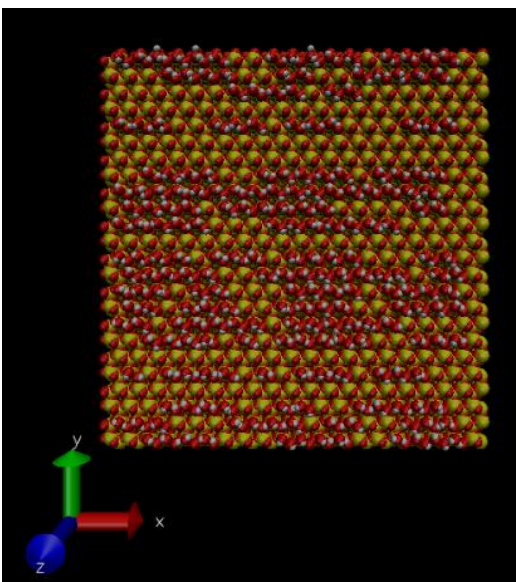


Figure showing 4.5 OH/nm² surface.