

A Molecular dynamic study of the impact of CO₂ flow on the wettability of a sandstone surface in response to pressure

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ABSTRACT

Reservoir wettability representing the competitive adsorption for different fluids on the surface, helps to predict the capture capacity and risk assessment for CO₂ geological sequestration. Numerous simulated models have been applied to reveal rock wettability with various pressures. However, most papers investigated the wettability alteration without considering CO₂ flow in the pores. There required an accurate model to describe the change in wettability of the reservoir during CO₂ injection. In this paper, the molecular simulation was conducted to investigate the wettability alteration of reservoirs during the CO₂ injection process. Considering the continuous CO₂ injection, we employed a model referring to quartz-CO₂-solution. In this model, CO₂ flow is regarded as a stationary layer. After that, we studied the wetting behavior of reservoirs with various pressures ranging from 0 MPa to 62.3 MPa. The results show that the contact angle first dramatically increases until 12.2 MPa from 67 °to 102.9 °and after that enters a ramp region and ultimately reaches a final value 120.7 °, which shows the CO₂ injection pressure weakens the water-wet property of reservoirs. Water clusters predicting the wettability are hard to move through the CO₂ atmosphere with the increase of pressure. Thus, the water cluster exhibits a hysteresis at a high pressure, resulting in the water cluster being hard to change and expend a long time to be equilibrated. Moreover, it is noted that the interaction of rock-CO₂ gradually increases with the increase of pressure, indicating that more CO₂ can be captured in tight sandstones. This paper proposed a model considering CO₂ flow in the CO₂ injection process, which can deepen the understanding of the wettability alteration in different CO₂ densities during CO₂ injection

for CO₂ geological sequestration, which further guides the operation of CO₂ in Carbon Capture, Utilization and Sequestration project.

Keywords: Tight sandstones, CO₂ sequestration, wettability, CO₂ injection, molecular dynamics simulation

1. INTRODUCTION

CO₂, as a major greenhouse gas, has had a significant impact on the ecological environment. Its effects include global warming, rising sea levels, and land desertification, among others. Therefore, it is crucial to control CO₂ emissions into the atmosphere in order to mitigate the harmful consequences associated with it. Recently, the Carbon Capture, Utilization, and Storage (CCUS) project has been proposed as a solution to reduce atmospheric CO₂ levels^[1-3]. The innovative concept of injecting CO₂ into reservoirs offers a promising approach to sequester CO₂ while simultaneously enhancing oil and gas production. This represents a win-win situation within the CCUS project, as it contributes to CO₂ reduction and benefits the oil and gas industry^[4-5].

The wettability of reservoirs plays a crucial role in the design and implementation of CO₂ injection projects. However, conducting laboratory experiments under extreme high temperatures and pressures presents significant challenges^[6-8]. Additionally, numerous factors can influence the wetting behaviors of reservoirs, making it difficult to isolate their individual effects. Furthermore, identifying wettability alteration in a real reservoir environment through

experimental means is also challenging. To overcome these limitations, molecular dynamics simulation (MD) has emerged as a valuable tool for investigating the changes in wetting behaviors during CO₂ injection^[9-10]. In particular, MD enables us to explore the underlying mechanisms of wettability alteration from a microscopic perspective. Despite numerous studies on CO₂-water-rock systems at different pressures, the continuous injection of CO₂ has received limited attention^[7-10]. Therefore, in this study, we conducted MD simulations to investigate the wettability alteration of CO₂-water-rock systems under various pressures during the CO₂ injection process. By analyzing contact angles, species concentrations, and interaction energies within the system, we can draw meaningful conclusions. This approach provides valuable insights for studying wettability alteration of reservoirs during CO₂ injection and can serve as a reference for future research in this area.

2. SIMULATION METHODOLOGY

2.1 CO₂/solution/rock molecular model

In this study, we employed Material Studio (MS) software to accomplish our objectives. We considered the CO₂ flow as a stationary layer and constructed a molecular model consisting of three layers: CO₂ layer, solution layer, and rock layer. The upper layer was created using the amorphous cell (AC) module, resulting in a 1.0 g/cm³ CO₂ layer. The middle layer incorporated a solution sphere surrounded by a CO₂ environment, each with varying densities. For the solution sphere, we utilized water molecules (400 H₂O), sodium ions (12 Na), and chloride ions (12 Cl) to construct a cubic layer with a density of 1.0 g/cm³ using the AC module. Subsequently, the cubic layer was transformed into a sphere with a radius of 15.0 Å. It is important to note that the sphere comprised 392 H₂O molecules and 12 NaCl molecules, fulfilling the requirements for a uniquely structured sphere with a fixed radius. We positioned the sphere at the centroid of an empty box measuring 44.22*42.55 in size. Following our experimental design, we introduced CO₂ at different densities into the remaining space of the empty box using a packing model. In the case of the rock model, we cleaved a quartz crystal model along the (0 0 1) direction and hydroxylated its surface to meet the desired quartz structure. Subsequently, we used the supercell module to create a 44.22*42.55 layer from the hydroxylated quartz model. By combining these three layers, we assembled a comprehensive

CO₂/solution/rock molecular model, as depicted in Fig. 1.

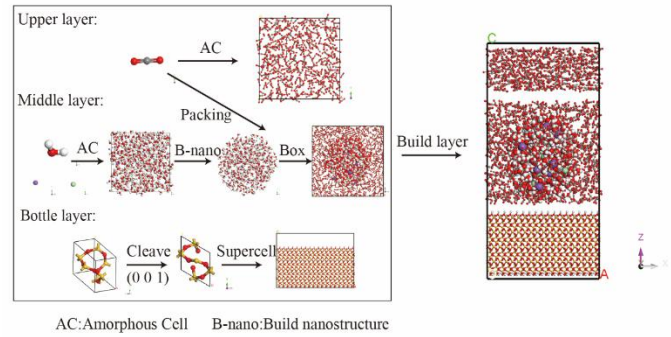


Fig. 1. The structure of CO₂/solution/rock molecular model

2.2 Simulation details

The objective of this study is to examine the impact of CO₂ on the wetting behavior of a sandstone system under varying pressure and temperature conditions. The first section focuses on investigating the influence of pressure. Using data from the NIST database and referring to Yu's paper^[4], we simulate different pressures by employing various CO₂ densities ranging from 0 to 1.0 g/cm³ at a temperature of 323 K, with increments of 0.2 g/cm³. Subsequently, the second section explores the effect of temperature, ranging from 323 K to 363 K in 10 K intervals, to uncover the wetting states of the CO₂/solution/rock system. It is important to note that in the CO₂/solution/rock molecular model, the CO₂ molecules in the upper layer and the quartz skeleton in the lower layer are fixed to create an immobile condition. On the other hand, the hydroxide radicals in the middle layer and the species in the bottle layer are free to move under the influence of the external environment.

Accurate force simulation is crucial for constructing a reliable model. Compass II, which combines Compass force with existing quantum mechanical calculations, is an ab initio force field commonly used for predicting the structure, energy, and dynamic changes in gas/condensed-phase properties. Given its effectiveness, Compass II force is widely employed in investigating dynamic interactions in rock-fluid systems. Further details on the Compass II force can be found in the relevant literature. Therefore, in this study, we employ the Compass II force.

3. RESULTS AND DISCUSSION

3.1 Wettability alteration owing to pressure of CO₂

The simulated equilibrium configurations of the CO₂/solution/rock system with different densities of the

CO₂ atmosphere are presented in Fig. 2. It is evident from Fig. 2 that as the CO₂ pressure increases, the contact angle of the quartz system gradually increases, indicating a change in the wettability of quartz. The variations in contact angle are illustrated in Fig. 3. Without the presence of CO₂, the initial wetting property of quartz exhibits a contact angle of 59.44°, indicating a water-wet characteristic in the quartz system. In fact, most of the simulated results indicate an initial contact angle of 22° for quartz. The higher contact angle observed in this study is attributed to the presence of the immobile CO₂ layer, which causes several water molecules from the water cluster to relocate, resulting in a higher contact angle compared to the other initial wetting properties. This confirms that the immobile CO₂ indeed affects the initial wetting property of quartz. At a pressure of 65 MPa, the contact angle reaches 112°, further demonstrating that the CO₂ atmosphere induces a transition of the quartz surface from water-wet to intermediate wetting. In other words, the CO₂ atmosphere reduces the water-wet property of quartz. Interestingly, we also observed a critical pressure of 12.2 MPa at which the wettability alteration occurs. When the pressure is below 12.2 MPa, the contact angle exhibits a significant increase. However, for pressures above 12.2 MPa, the contact angle shows a slower rate of increase. This result aligns with the trend observed in a previous study conducted by Yu^[4]. Despite using the same pressure and temperature values, there are differences between our model and Yu's results^[4]. These disparities arise from variations in the solution concentration and the presence of a barrier. In Yu's study, the barrier consisted of a graphene baffle^[4], while in our study, an immobile CO₂ layer was used.

It is important to note that the contact angle is highly sensitive to the CO₂ environment. As depicted in Fig. 3a and Fig. 3b, it can be observed that an initial contact angle of 180° is more prone to change and reaches an equilibrium state more rapidly in a lower CO₂ environment. With increasing CO₂ density, the movement of water clusters through the CO₂ atmosphere becomes more challenging. Consequently,

water clusters exhibit hysteresis under high CO₂ pressure, resulting in a slower rate of change and requiring more time to reach equilibrium. The significance of this hysteresis is that a high CO₂ environment may impede fluid flow, and the resistance of CO₂ to fluid movement should be taken into consideration in real reservoir scenarios.

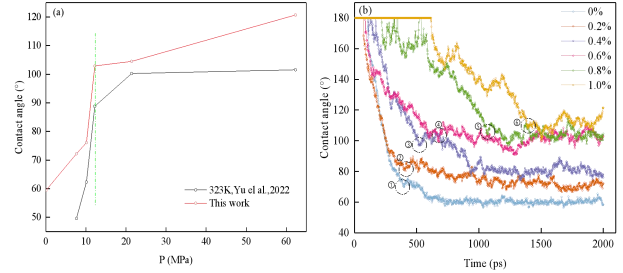


Fig. 3. The contact angle results. (a) contact angle with pressure; (b) dynamic contact angle with time.

3.2 Changes in relative concentration of species

Conducting a comprehensive analysis of the species alteration is crucial for enhancing the understanding of wettability changes in the quartz system within a CO₂ environment. In our system, the species encompass CO₂ molecules, H₂O molecules, Na ions, and Cl ions. Thus, we conducted individual analyses for each species to elucidate their behavior. Relative concentration, which accurately describes the positional changes in response to the external CO₂ atmosphere, was utilized. The initial z direction is considered as the location of the quartz surface (24 Å). The relative concentrations of the various species are illustrated in Fig. 4.

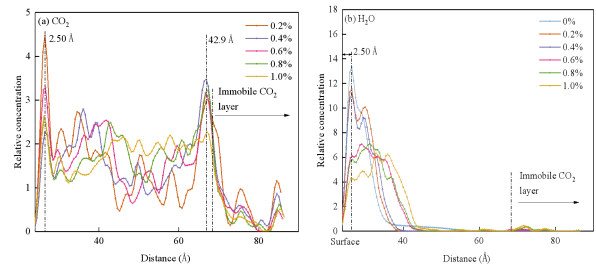


Fig. 4. The relationships between concentration of species and distance. (a) CO₂; (b) H₂O.

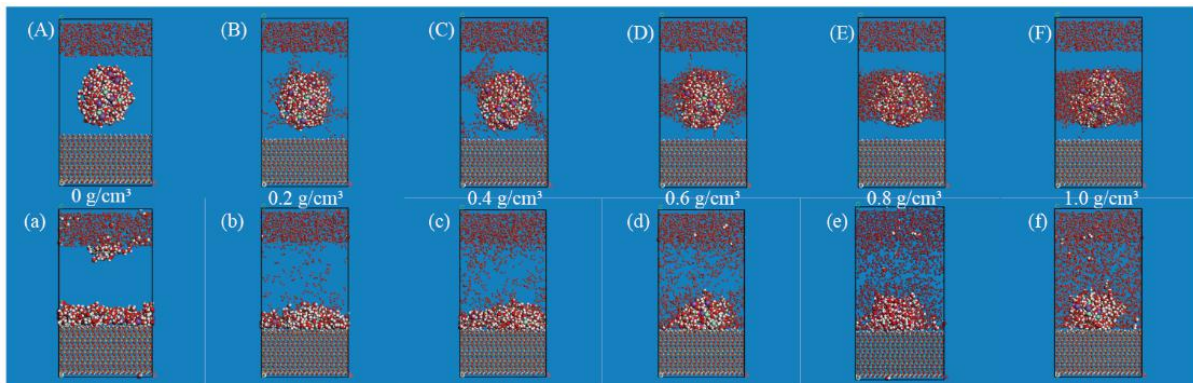


Fig. 2. Equilibrated states of CO₂/solution/rock system at various pressures

From the observations in Fig. 4, it is evident that distances greater than 68.4 Å correspond to the location of the immobile CO₂ layer. The presence of CO₂ and H₂O species within this region suggests that these species are able to traverse through the immobile CO₂ layer, thereby influencing their distribution. This finding underscores the importance of constructing accurate models for simulating real reservoirs. Additionally, it provides further support for the use of an immobile CO₂ layer instead of a graphene baffle in the model construction, as it has a more significant impact on the system dynamics.

3.3 Changes in the interaction energies of system

To elucidate the mechanisms underlying wettability alteration at different pressures, we measured the interaction energies between rock-CO₂, rock-water, and CO₂-water, as illustrated in Fig. 5. The calculation of the interaction energy is based on Equation 1, which is presented below.

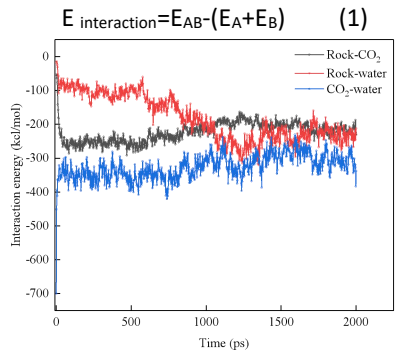


Fig. 5. The interaction energies and time

Fig. 5 demonstrates that the interaction energy of the rock-water system decreases over time, while the interaction energies of the rock-CO₂ system and CO₂-water system initially increase and eventually stabilize. Notably, the overall trend of the interaction energies indicates that the rock-water interaction energy decreases, leading to the departure of water from the rock surface and consequently causing a decline in the hydrophilic property. Furthermore, it is noted that the interaction of rock-CO₂ system and CO₂-water system gradually increases with the increase of pressure, indicating that more CO₂ can be captured in tight sandstones. This observation strongly supports the idea that the reduction in the rock-water interaction plays a pivotal role in the weakening of the water-wet property.

4. CONCLUSIONS

In this study, we conducted molecular simulations to investigate the wettability alteration of reservoirs

during the process of CO₂ injection. By considering the continuous flow of CO₂, we treated it as a stationary layer. Subsequently, we examined the wetting behaviors of reservoirs under different pressure conditions. Based on our thorough analysis, the following conclusions can be drawn.

- (1) the contact angle initially experiences a significant increase, rising from 67° to 102.9° until a pressure of 12.2 MPa. Subsequently, it enters a gradual transition phase and eventually reaches a final value of 120.7°. This finding indicates that the pressure resulting from CO₂ injection weakens the water-wet property of reservoirs.
- (2) As the pressure increases, water clusters, which serve as indicators of wettability, encounter greater difficulty in traversing the CO₂ atmosphere. Consequently, water clusters exhibit hysteresis at high pressures, leading to prolonged equilibration times and making it challenging for the water cluster to undergo changes.
- (3) the interaction energy of the rock-water system decreases, indicating a weakening of the interaction between the rock surface and water molecules. Conversely, the interaction energies of the rock-CO₂ system and CO₂-water system initially increase and eventually reach a stable state. This trend suggests that the presence of CO₂ influences the interactions between the rock surface and CO₂ molecules, as well as between CO₂ and water molecules.

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DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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