

# INFLUENCE OF PH ON THE WETTABILITY OF CARBONATE ROCKS FOR CARBON DIOXIDE SEQUESTRATION IN DEEP SALINE AQUIFER

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## ABSTRACT

*The escalating carbon dioxide (CO<sub>2</sub>) emissions have precipitated climate change, underscoring the urgent need for innovative solutions. Carbon Capture and Storage (CCS) represents a groundbreaking technology to mitigate carbon emissions by capturing CO<sub>2</sub> and depositing it deep within reservoirs. This study focuses on the storage aspect of CCS by scrutinising reservoir properties. A pivotal factor influencing the geological storage of CO<sub>2</sub> is the wettability of the rock/CO<sub>2</sub>/brine system, which is intricately linked to the contact angle. However, previous research has indicated that pH can significantly influence the wettability of this system. Acetic acid, a prevalent organic acid in the petroleum industry, is commonly encountered and serves as a means to modulate pH. This experiment investigates pH variations, ranging from 3 to 7, through the introduction of acetic acid, while maintaining a salinity level of 30,000 ppm. Additionally, the type of rock mineral plays a crucial role in these findings. Therefore, this paper emphasises carbonate rocks, with a particular focus on limestone composed primarily of calcium carbonate (CaCO<sub>3</sub>). The experiment is conducted under elevated supercritical conditions, encompassing pressures of 10 MPa and 15 MPa, along with temperatures of 305 K and 323 K. Equilibrium contact angles are determined by measuring receding and advancing angles using the Vinci IFT 700 instrument under supercritical conditions. The results reveal a consistent trend wherein contact angles decrease as pH, temperature, and pressure increase, indicating a shift towards a water-wet system at higher pH, temperature, and pressure levels.*

**Keywords:** Carbon Capture and Storage (CCS), Wettability, Contact angle, pH, Acetic acid, Salinity, Carbonate rocks, Limestone, Supercritical conditions

## INTRODUCTION

In the backdrop of the modern industrial era, human-driven carbon dioxide (CO<sub>2</sub>) emissions have triggered a pronounced surge in atmospheric CO<sub>2</sub> concentration [1]. The consequences of this surge are starkly evident, with global temperatures on an upward trajectory, soaring from 275 ppm to 370 ppm since the onset of the 19th century [2]. As of May 2022, measurements by the National Oceanic and Atmospheric Administration (NOAA) indicate that CO<sub>2</sub> levels have surged to 421 ppm [3]. This surge in CO<sub>2</sub> emissions has initiated a detrimental chain reaction, as CO<sub>2</sub> accumulates in the atmosphere, trapping heat and instigating global warming [4]. The repercussions of global warming manifest in various ways, including rising sea levels, ocean acidification, and threats to biodiversity [5]. In response to this pressing crisis, Carbon Capture and Storage (CCS) has emerged as a forefront technology.

CCS stands as a pivotal technology that entails capturing CO<sub>2</sub> emissions and subsequently conveying them via various means such as trucks, pipelines, and trains to subterranean storage sites [6]. These storage sites encompass depleted hydrocarbon reservoirs, deep saline aquifers, and coal beds [7]. Numerous factors come into play in the underground storage of CO<sub>2</sub>, including porosity, permeability, temperature, pressure, wettability, and rock mineral composition [8]-[9]. CO<sub>2</sub> is injected into these reservoirs at supercritical pressure and temperature conditions to maximise storage capacity, typically at 7.38 MPa and 31.04°C [10]. In the case of reservoirs with depths exceeding 800 meters, underground conditions typically surpass the critical point of CO<sub>2</sub>, resulting in supercritical conditions that optimise dense CO<sub>2</sub> storage capacity [11].

Salinity and pH values emerge as critical factors impacting the wettability of the rock/CO<sub>2</sub>/brine system, with a direct correlation to the contact angle, which is a key determinant of wettability [12]. Meanwhile, the composition of the reservoir rock, categorised into igneous, metamorphic, and sedimentary types, plays a pivotal role in CO<sub>2</sub> sequestration. Among these, sedimentary rocks, including limestone, dolomite, and evaporite, predominate in most reservoirs [13]. Within the context of pH values, the presence of organic acids, particularly acetic acid, is widespread in petroleum basins worldwide when mixed with water. Acetic acid, with the chemical formula CH<sub>3</sub>COOH, contributes H<sup>+</sup> ions to the fluid composition [14]. Notably, the length of the acid chain can determine whether the rock surface exhibits oil-wet or water-wet characteristics, with short-chain acids favouring water-wet conditions [15].

Given the limited body of research on the influence of pH on the wettability of carbonate, this paper embarks on an exploration of limestone wettability by varying the pH of acetic acid (ranging from pH 3 to 7). The experimentation is conducted under elevated supercritical conditions, with temperatures set at 305 K and 323 K, and pressures at 10 MPa and 15 MPa, respectively. Throughout the preparation of varying acetic acid concentrations, brine salinity remains consistent at 30,000 ppm as a baseline. The research's primary objective is to ascertain the receding and advancing angles utilising the interfacial tension machine (IFT 700), thereby elucidating the impact of pH on system wettability under heightened supercritical conditions. Notably, a lower pH value (<5) is expected to result in a strongly water-wet system, driven by the adsorption of H<sup>+</sup> ions [16]. Such water-wet reservoirs are deemed more conducive to CO<sub>2</sub> storage in terms of capacity and security [7].

As previously mentioned, the upsurge in CO<sub>2</sub> emissions stemming from human activities has culminated in a critical environmental predicament, marked by the entrapment of heat and detrimental repercussions. To address this pressing issue, CCS technology has emerged as a pivotal means of curtailing CO<sub>2</sub> emissions by capturing, conveying, and securely storing CO<sub>2</sub> underground. Within the realm of CCS, this paper delves predominantly into the storage facet, with a particular emphasis on an underexplored domain—namely, the influence of pH values on wettability within limestone reservoirs under elevated supercritical conditions.

While a plethora of studies have examined CO<sub>2</sub> sequestration within reservoirs across various parameters, the impact of pH values on wettability in limestone reservoirs at heightened supercritical conditions remains relatively uncharted. In this pursuit, the central parameters scrutinised are pH, salinity, pressure, and temperature, all of which exert a substantial influence on system wettability. It's essential to note that limestone mineral composition typically encompasses calcite, dolomite, and assorted impurities [16]. Importantly, most limestone reservoirs boast adequate permeability and porosity, making them well-suited for accommodating substantial volumes of CO<sub>2</sub> [17].

Furthermore, pH values wield a substantial impact on the wettability of the CO<sub>2</sub> sequestration system. Acetic acid, a prevalent organic acid found in numerous petroleum basins stands out as a key factor [14]. Being a short-chain acid, acetic acid lends itself to the effective storage of CO<sub>2</sub> due to its propensity for water-wetting characteristics [7]. Studies have indicated that lower pH levels result in a pronounced water-wet system, primarily driven by the adsorption of H<sup>+</sup> ions [16]. Consequently, the pH values play a pivotal role in determining system wettability, thereby exerting a significant influence on CO<sub>2</sub> storage behaviour [12].

With these considerations in mind, this research endeavours to probe the shifting dynamics of contact angles within the rock/CO<sub>2</sub>/brine system, offering valuable insights into the CO<sub>2</sub> storage potential under supercritical pressure and temperature conditions. To this end, the study focuses on the determination of receding and advancing angles by modulating pH values in the range of 3 to 7 using acetic acid. Notably, the preparation of the experimental solutions deviates from conventional practice, with 30,000 ppm of NaCl brine serving as the base instead of water. Ultimately, the experiment is conducted under elevated supercritical pressures and temperatures, specifically 10 MPa, 15 MPa, 305 K, and 323 K, in a bid to simulate the intricate underground conditions pertinent to CO<sub>2</sub> storage.

The preceding sections have underscored the imperative need for this research endeavour. In light of the challenges posed by escalating CO<sub>2</sub> emissions and their far-reaching consequences, the primary objective of this study is to ascertain the contact angle

between rock-CO<sub>2</sub> and rock-brine interfaces—a critical determinant impacting CO<sub>2</sub> sequestration within limestone reservoirs operating under supercritical conditions.

Notably, recent research has established that wettability gauged through the measurement of contact angles, serves as a vital indicator of surface hydrophobicity and hydrophilicity [18]. Furthermore, emerging insights indicate that pH values within reservoirs wield a substantial influence on wettability dynamics [19]. Therefore, it is incumbent upon us to thoroughly investigate the impact of varying pH values, particularly under the crucible of heightened pressure and temperature conditions, on limestone samples. This investigation is poised to shed light on the alterations in wettability, which, in turn, have profound implications for the capacity of CO<sub>2</sub> storage within these reservoirs.

With these overarching objectives in mind, this paper is framed by the following specific aims:

1. To rigorously evaluate the contact angle between the rock/CO<sub>2</sub>/brine interfaces, thereby offering insights into the surface wettability of limestone. This assessment encompasses varying pH levels, ranging from 3 to 7, while subjecting the samples to elevated supercritical temperatures of 305 K and 323 K, along with pressures of 10 MPa and 15 MPa.
2. To discern the efficacy of CO<sub>2</sub> storage, measured in terms of its capacity and feasibility, contingent upon fluctuations in pH levels (ranging from 3 to 7) under the influence of elevated supercritical temperatures (305 K and 323 K) and pressures (10 MPa and 15 MPa).

These objectives collectively form the cornerstone of the inquiry, aiming to unravel the intricate interplay between pH values, wettability, and CO<sub>2</sub> storage capacities within limestone reservoirs operating in supercritical conditions.

### Carbon Capture and Storage (CCS)

Geological sequestration plays a pivotal role in the field of CCS. The targeted underground reservoirs for CO<sub>2</sub> sequestration include deep saline aquifers, coal beds, and depleted oil & gas reservoirs [20]. The primary focus is on the deep saline aquifer, which is renowned for its superior CO<sub>2</sub> storage capabilities when compared to coal beds and depleted oil and gas reservoirs [20].

Notably, the global landscape of CCS is witnessing active development, with twenty-two large-scale CCS projects currently underway worldwide [21].

### Type of Reservoirs for CO<sub>2</sub> Sequestration

Reservoir types are pivotal considerations in the context of CO<sub>2</sub> geological storage, offering diverse options for effective carbon sequestration [7]. These reservoirs serve as essential platforms for isolating CO<sub>2</sub> and mitigating atmospheric carbon levels through trapping mechanisms.

In a study conducted by Alafnan [22], the utilisation of depleted heavy oil reservoirs for CO<sub>2</sub> storage was explored. Depleted reservoirs, which have held high-pressure hydrocarbons for extended periods before production, possess the potential for long-term CO<sub>2</sub> geological storage via dissolution in residual oil. Reservoirs featuring high asphaltene residuals can effectively store CO<sub>2</sub> in sorbed form. The presence of asphaltene increases with depletion rates, leading to the formation of a thin asphaltene film on the rock surface that acts as a medium for CO<sub>2</sub> sequestration. This study employed four aromatic carbon structures to estimate CO<sub>2</sub> storage capacity under subsurface conditions with a pressure of 20.67 MPa and a temperature of 305 K. The research highlights the correlation between absorption rates and pressure while emphasising the independence of the asphaltene molecular structure.

In a separate investigation by Edem et al. [23], CO<sub>2</sub> storage within deep saline aquifers was examined. The study employed a homogeneous quartz-based sandstone core sample measuring 3 inches in length and 1 inch in diameter. Experiments were conducted under supercritical conditions with pressure set at 7.38 MPa and temperature at 31.1°C. Brine solutions, including NaCl, KCl, and CaCl<sub>2</sub>, were prepared at concentrations of 5, 10, 15, 20, and 25 wt%. The core flooding method was employed to assess CO<sub>2</sub> injectivity. Results revealed that salinity levels between 10% and 20% exhibited the highest efficiency in CO<sub>2</sub> storage. Increased brine density, however, led to reduced CO<sub>2</sub> storage capacity due to hindered gas flow. Additionally, the solubility of salts in water also played a role in CO<sub>2</sub> storage within deep saline aquifers, with less soluble salts prone to precipitation compared to those with higher solubility.

Conversely, Chalbaud et al. [24] researched the interfacial properties associated with CO<sub>2</sub> storage in deep saline aquifers. These properties encompassed wettability, interfacial tension, capillarity, and interfacial mass transfer, all of which exerted substantial influence on fluid distribution in porous media and the CO<sub>2</sub> storage system. The experiments were conducted across varying temperature, pressure, and salinity conditions. Pressure ranged from 45 bars to 225 bars, temperatures encompassed 27°C, 71°C, and 100°C, and brine salinities of 5,000 ppm, 50,000 ppm, 100,000 ppm, and 150,000 ppm of NaCl were utilised. The findings revealed that CO<sub>2</sub> partially wets the surface, leading to reduced capillary pressure when the surface exhibits water-wet or oil-wet characteristics.

These studies collectively provide valuable insights into diverse aspects of CO<sub>2</sub> geological storage, shedding light on the potential of various reservoir types and the interplay of key properties in the storage process.

### Trapping Mechanisms

Trapping mechanisms play a pivotal role in the context of CO<sub>2</sub> geological sequestration, as they govern both the effectiveness and security of stored CO<sub>2</sub> over time. These mechanisms encompass structural trapping, solubility trapping, residual trapping, and mineral trapping.

To begin, structural trapping hinges on the presence of impermeable caprocks atop the reservoir, serving as a formidable barrier to CO<sub>2</sub> escape. Caprocks typically comprise materials with extremely low permeability, such as shales, mudrock, clay, and tight carbonates [25]. When CO<sub>2</sub> is injected into the reservoir, it undergoes upward migration and accumulates within the caprock region, primarily driven by buoyancy forces [26]. This buoyant CO<sub>2</sub>, however, encounters the caprock's impermeable seal, effectively preventing it from ascending to upper zones and thus safeguarding the long-term retention of CO<sub>2</sub> within the formation [25]. Structural trapping thus establishes a robust barrier against CO<sub>2</sub> escape, with caprocks acting as sentinels to confine and secure the stored CO<sub>2</sub> within the reservoir. Secondly, residual trapping involves the entrapment of injected CO<sub>2</sub> within the capillary pores of the rock [26]. When CO<sub>2</sub> is introduced into the reservoir, it displaces brine through a co-current displacement mechanism. Following injection, the upward movement of gas

bubbles occurs, and as these bubbles ascend, their CO<sub>2</sub> concentration gradually diminishes, thus augmenting the residual trapping process [26]. However, if injection ceases, CO<sub>2</sub> begins to migrate upwards while brine, owing to differences in density, moves downward.

In essence, residual trapping is a vital mechanism wherein CO<sub>2</sub> is sequestered within the minute pores of the rock, and its fate is influenced by the dynamic interplay of various factors, including buoyancy and density gradients.

On the other hand, solubility trapping is a process that involves the dissolution of CO<sub>2</sub> within the liquid phase. Solubility has a profound impact on the overall CO<sub>2</sub> storage capacity [27]. When supercritical CO<sub>2</sub> is injected into deep reservoirs, it undergoes dissolution within the existing brine, leading to an increase in brine density. This change in brine density, in turn, triggers mineral trapping mechanisms, as denser brine causes it to sink under the influence of gravitational forces. The solubility of CO<sub>2</sub> can be investigated by considering factors such as pH, pressure, and the migration patterns of CO<sub>2</sub> [28].

Solubility trapping represents a critical facet of CO<sub>2</sub> sequestration, as it elucidates how the dissolution of CO<sub>2</sub> in brine can affect both storage capacity and the subsequent behaviour of the CO<sub>2</sub> within the reservoir. The fourth trapping mechanism is mineral trapping, renowned for its enduring and highly secure nature in CO<sub>2</sub> storage through the precipitation of carbonate minerals [29]. Mineral trapping varies depending on the reservoir's mineral composition and the characteristics of pore fluids [26]. This process unfolds as the brine, enriched with dissolved CO<sub>2</sub>, experiences increased density and descends under the influence of gravity, leading to the onset of mineral trapping. When the injected CO<sub>2</sub> dissolves in brine, it gives rise to weak carbonic acid, which subsequently reacts with the minerals present, ultimately resulting in the formation of carbonate minerals. Consequently, the mineral trapping mechanism operates over an extended period, contributing to the long-term security and permanence of CO<sub>2</sub> storage.

### CCS on Carbonate Reservoir

Xie et al. [16] investigated the impact of pH on the wettability of the oil/brine/carbonate system, with the study encompassing carbonate rocks such as limestone

and dolomite. Contact angle measurements were performed in the presence of calcium chloride (CaCl<sub>2</sub>) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) under conditions of pH 3 and 8. The experimentation utilised the Vinci IFT-700 apparatus, maintaining a temperature of 25°C, 60°C, and 100°C, and a constant pressure of 100 bar (10 MPa). The results of this study revealed that lower pH values (<5) induce a pronounced water-wetting effect, attributed to H<sup>+</sup> ion adsorption at the interface.

In the research conducted by Mwangi et al. [15], the focus was on examining the influence of organic acids on the wettability of both sandstone and carbonate rocks. The carbonate rocks under investigation included Silurian dolomite, Indiana limestone, and Austin chalk. Wettability assessments were carried out using different types of acids, namely acetic acid (short-chain), naphthenic acid (long-chain), and myristic acid (long-chain). Experimental conditions entailed temperatures of 23°C, 70°C, and 100°C, with varying salinity levels ranging from 0 to 100,000 ppm. The findings from this study indicated that short-chain acids and higher temperatures contribute to increased water-wetting characteristics in carbonate rocks.

In contrast, Yekeen et al. [30] delved into an exploration of the influential factors affecting the wettability of the rock/CO<sub>2</sub>/brine system. Among these factors, temperature and pressure emerged as critical determinants. Critical reviews revealed that at elevated temperatures, the contact angle decreases, thereby enhancing storage capacity and security. Conversely, critical reviews also indicated that as pressure increases, the contact angle tends to rise. However, it is important to note that this assessment exclusively considered the rock/CO<sub>2</sub>/brine system in the context of temperature and pressure; pH variations were not accounted for within the scope of the experiment.

**METHODOLOGY**

The experiment's design revolves around the careful consideration of variables that can influence the outcomes. To ensure precision and clarity in the project framework, the following variables were identified: pH, pressure, temperature, and the method employed, which involved the use of the Vinci IFT 700 machine through the sessile drop method.

**Table 1** Variable of the experiment

pH	Salinity (ppm)	Pressure (MPa)	Temperature (K)	Method
3	30,000	10 15	305 323	Tilted plate (17°)
4				
5				
6				
7				

In accordance with Table 1, the experiment was carried out by varying the pH of the brine across five different levels, maintaining a constant salinity of 30,000 ppm, and conducting trials at two different pressures and two temperatures. The tilted angle for the method remained fixed at 17° throughout the experiment. The variables can be succinctly categorised as follows:

1. Independent variables: pH, temperature, and pressure
2. Dependent variable: Contact angles of the system
3. Constant variables: Salinity, tilted angle, type of salt, and type of rock

**Contact Angle Measurement**

In this experiment, the IFT 700 interfacial tension meter was employed to measure the advancing and receding angles using the sessile drop method. The tilted angle chosen for the limestone sample was set at 17°, consistent with previous studies [7].



**Figure 1** IFT-700 machine

The IFT 700 meter features a chamber volume of 1 × 10<sup>-5</sup> m<sup>3</sup> and is capable of operating at temperatures up to 180°C and pressures up to 68.9 MPa. Additionally, the device is connected to a computer equipped with

a camera capable of executing the sessile drop method. A software program known as Drop Analysis Software (DAS) was utilised to record the droplet's shape.



Figure 2 Illustration of sample set-up

Figure 2 provides an illustrative depiction of the sample setup within the chamber. The limestone sample was positioned on the 17° tilted mould and securely inserted into the holder. Subsequently, the chamber was tightly sealed following the placement of the sample to facilitate measurement procedures.

## RESULTS AND DISCUSSION

The rock samples underwent X-ray diffraction (XRD) analysis to determine their mineral composition.

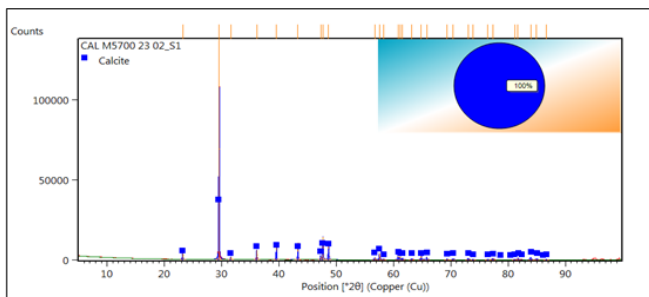


Figure 3 XRD of the sample

The XRD results were subsequently analysed to identify the mineral. Matching was performed by

comparing the obtained results with data available in the HighScore Plus application. A set criterion for composition identification was established: peaks that matched with the library data three times or more were considered. The matching process concluded when the peak arrows were no longer visible at the top.

In Figure 3, the XRD result for one of the samples is displayed, indicating that the mineral composition consists of 100% calcite, which is primarily composed of calcium carbonate ( $\text{CaCO}_3$ ). Therefore, the tested sample was definitively identified as limestone. Subsequently, the sample was appropriately sized for contact angle measurements.

The advancing and receding angles were gauged using an online protractor. It's important to note that each sample underwent measurement three times to enhance the accuracy of the values obtained. In this section, the authors provide an illustrative example at pH 3, 305 K, and 10 MPa.

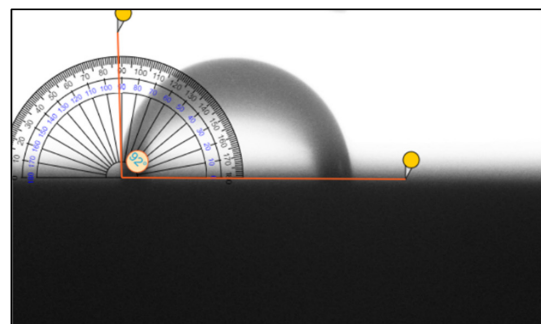


Figure 4 Advancing angle of pH 3 at 305 K and 10 MPa

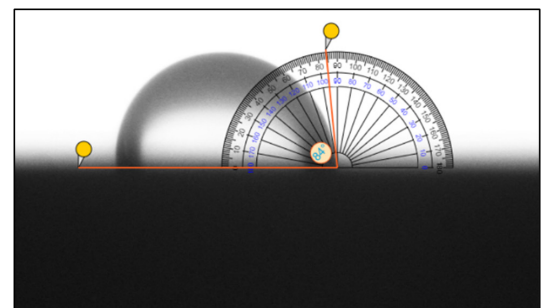


Figure 5 Receding angle of pH 3 at 305 K and 10 MPa

Following the determination of advancing and receding angles, these values were incorporated into the equation to calculate the equilibrium contact angle. For instance, Figures 4 and 5 exhibit advancing and receding angles of 92° and 84°, respectively, for the given conditions.

Table 2 Overall results

Temperature (K)	Pressure (MPa)	pH	Advancing Angle (°)	Receding Angle (°)	rA	rR	Equilibrium Angle (°)
305	10	7	117	101	0.600	0.717	108.10
305	15		104	96	0.696	0.752	99.82
323	10		102	93	0.710	0.773	97.29
323	15		94	89	0.766	0.801	91.44
305	10	6	105	100	0.689	0.724	102.43
305	15		99	94	0.731	0.766	96.44
323	10		95	88	0.759	0.808	91.39
323	15		89	85	0.801	0.828	86.97
305	10	5	103	97	0.703	0.745	99.90
305	15		96	93	0.752	0.773	94.48
323	10		94	86	0.766	0.821	89.86
323	15		87	84	0.814	0.835	85.48
305	10	4	94	85	0.766	0.828	89.33
305	15		86	84	0.821	0.835	84.99
323	10		85	77	0.828	0.885	80.89
323	15		83	75	0.842	0.899	78.90
305	10	3	92	84	0.780	0.835	87.87
305	15		85	83	0.828	0.842	83.99
323	10		84	75	0.835	0.899	79.37
323	15		82	73	0.849	0.913	77.38

Contact Angle Analysis

The data presented in Table 2 was utilised to generate several graphs for further analysis. The primary parameters under consideration are pH, pressure, temperature, and equilibrium contact angle.

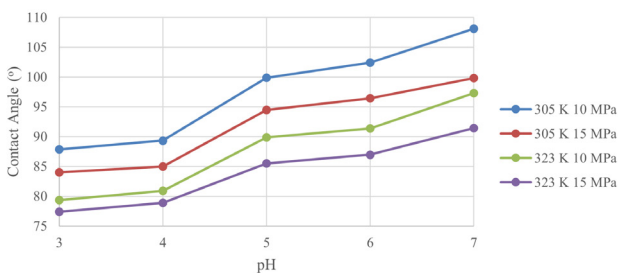
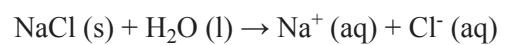


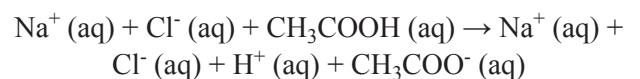
Figure 6 Contact angle vs. pH at different temperatures and pressures

Figure 6 illustrates the relationship between contact angles and pH at varying pressures and temperatures. As shown in the plot, contact angles tend to decrease as pH values decrease from pH 7 to pH 3, regardless of the pressure and temperature conditions.

To better comprehend the reactions involved, it's essential to examine the chemical equations. The brine solution was prepared by dissolving sodium chloride (NaCl) salt in water at a concentration of 30,000 ppm:



This equation represents the dissolution of solid NaCl in water, resulting in the formation of sodium ions (Na<sup>+</sup>) and chloride ions (Cl<sup>-</sup>), with water molecules surrounding the ions. Following the preparation of the brine solution, acetic acid was introduced to control the pH:



The addition of acetic acid to the sodium chloride brine solution leads to the formation of various ions, including sodium ions (Na<sup>+</sup>), acetate ions (CH<sub>3</sub>COO<sup>-</sup>),

hydrogen ions ( $H^+$ ), and chloride ions ( $Cl^-$ ). It's important to note that the  $H^+$  ions do not react with  $Cl^-$  ions to form  $HCl$ . This is because acetic acid is a weak acid and only partially dissociates into  $H^+$  ions and  $CH_3COO^-$  ions. As a result, the concentration of  $H^+$  ions remains relatively low, and  $Cl^-$  ions are more likely to exist as free ions in the solution due to their stability.

Moving on to the limestone, the XRD results indicate a composition primarily composed of calcite ( $CaCO_3$ ). Calcite is an ionic compound consisting of calcium ions ( $Ca^{2+}$ ) and carbonate ions ( $CO_3^{2-}$ ).

To gain a deeper understanding of the contact angle trends with pH, it's important to consider the chemical interactions involved. When the solution contains  $Na^+$ ,  $CH_3COO^-$ ,  $H^+$ , and  $Cl^-$  ions interacting with  $Ca^{2+}$  and  $CO_3^{2-}$  ions on the limestone surface, the  $H^+$  ions protonate the limestone surface by donating protons. Protonation weakens the repulsion between the limestone surface and the negatively charged ions, allowing them to come closer and increasing the attractive forces between the surface and the solution. In other words, protonation imparts a more positive charge to the surface, which in turn attracts both  $Cl^-$  and  $CH_3COO^-$  ions, reducing the repulsion force. It's worth noting that while the pH was adjusted using acetic acid to prepare different pH levels of sodium chloride brine, the salinity remained constant at 30,000 ppm. Therefore, the concentrations of  $Na^+$  and  $Cl^-$  ions remained the same for all brine solutions. Theoretically, lower pH levels require more acetic acid, leading to higher concentrations of  $CH_3COO^-$  and  $H^+$  ions at lower pH levels. This increased presence of  $H^+$  ions enhances the protonation process, further reducing the repulsion force between the fluid and the surface and increasing hydrophilicity. Consequently, contact angles decrease due to increased hydrophilicity between the fluid and the surface.

Another significant factor influencing contact angle is temperature. As such, the experiment was conducted at elevated temperatures for further evaluation.

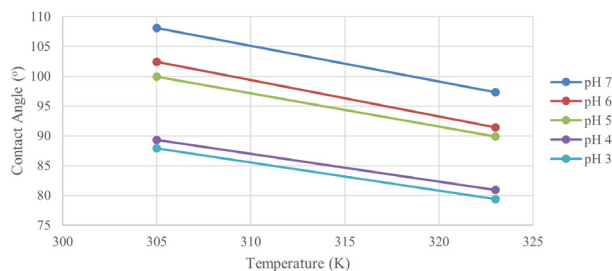


Figure 7 Contact angle vs. temperature at 10 MPa

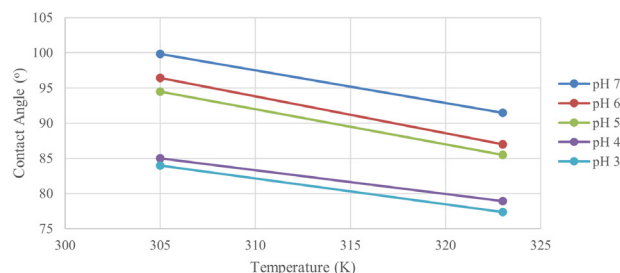


Figure 8 Contact angle vs. temperature at 15 MPa

Figures 7 and 8 depict the contact angle plotted against temperature at 10 MPa and 15 MPa, respectively. Both results show a consistent trend: the contact angle decreases as the temperature increases from 305 K to 323 K, regardless of the pH level. This behaviour can be attributed to the increase in kinetic energy and molecular thermal activity with higher temperatures.

As temperature rises, molecules gain more kinetic energy and move more rapidly, which reduces cohesive forces between them. As a result, the surface tension decreases because surface tension is a measure of cohesive forces among molecules. Lower surface tension leads to a lower contact angle or increased spreading of water between the droplet and the surface.

In addition to temperature, the experiment was conducted at elevated pressures ranging from 10 MPa to 15 MPa. Two graphs were generated to illustrate the relationship between contact angle and pressure.

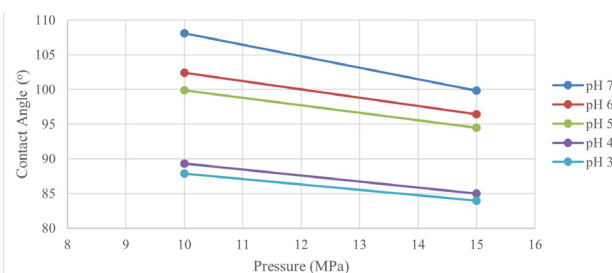
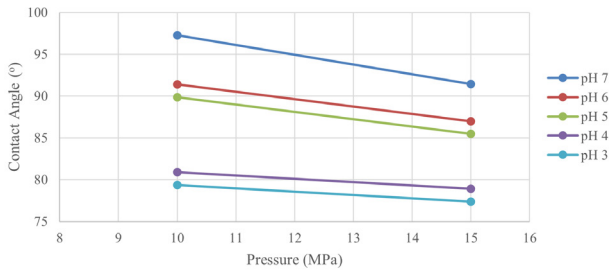


Figure 9 Contact angle vs. pressure at 305 K





**Figure 10** Contact angle vs. pressure at 323 K

Both Figures 9 and 10 depict the contact angle as a function of pressure at two different temperatures, 305 K and 323 K. In both cases, the results consistently indicate that the contact angle decreases as pressure increases from 10 MPa to 15 MPa, regardless of the pH level.

This phenomenon can be explained by considering the behaviour of a liquid droplet on a solid surface when subjected to increased pressure. As pressure mounts on the droplet, it becomes compressed and flattened, leading to a reduction in the contact angle. The increased pressure causes the droplet to spread out over a larger surface area, thereby increasing the total area of contact between the droplet and the surface. This, in turn, enhances the adhesive forces between the droplet and the surface, resulting in a lower contact angle and a greater propensity for the surface to become more water-wet under higher pressure conditions.

In summary, this section has explored and presented insights into three significant factors: pH, temperature, and pressure, all of which influence contact angle. The lowest contact angle observed among all the samples occurred at pH 3, 323 K, and 15 MPa, which aligns with the explanations provided above. Specifically, the lower contact angle at pH 3 can be attributed to a reduced repulsion force between the surface and the droplet due to the increased protonation driven by a higher concentration of  $H^+$  ions. Additionally, higher temperature reduces cohesive strength and surface tension, facilitating easier droplet spreading, while elevated pressure increases adhesive forces between the droplet and the surface, ultimately leading to reduced contact angles.

## CONCLUSION

In this study, the authors thoroughly investigated the wettability of limestone surfaces, exploring the nuanced interactions influenced by varying pH levels, temperatures, and pressures. The analysis uncovered intricate dynamics between these variables and their collective impact on surface wettability. Noteworthy findings include the pH-dependent trend, where lower pH values, particularly at pH 3, yielded the lowest contact angles due to protonation by  $H^+$  ions, weakening repulsion forces and enhancing hydrophilicity. Elevated temperatures, ranging from 305 K to 323 K, consistently reduced contact angles, elucidating the role of heightened kinetic energy and molecular thermal activity in diminishing cohesive forces. Additionally, increasing pressure from 10 MPa to 15 MPa resulted in lower contact angles, attributed to pressure-induced droplet compression and enhanced adhesive forces, ultimately rendering the limestone surface more water-wet. These insights contribute to a comprehensive understanding of the multifaceted factors influencing surface wettability.

Several recommendations are proposed to enhance the robustness and applicability of the findings presented in this paper. Firstly, diversifying experimental methods, particularly by incorporating alternative techniques such as the captive bubble method alongside the sessile drop technique, is advised. This approach can provide a more thorough and validated assessment of surface wettability trends. Expanding the experimental parameters by conducting studies at higher pressures and temperatures will contribute to a broader understanding of surface wettability under diverse geological conditions. Additionally, exploring the effects of other organic acids beyond acetic acid on surface wettability can offer valuable insights into the nuanced role of acidity in fluid-rock interactions. Lastly, the development of  $CO_2$  storage simulation models is recommended to unravel the underlying mechanisms and principles governing wettability alterations in subsurface geological formations. These models will enable researchers to simulate various scenarios, predict outcomes, and refine their understanding of the complex processes involved in  $CO_2$  storage. By implementing these suggestions, researchers can elevate the depth and breadth of knowledge surrounding surface wettability in geological contexts, particularly in the context of carbon storage.

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