Advances in
Geo-Energy Research

Vol. 17, No. 1, p. 43-55, 2025

Original article

Experimental investigation of CO_2 residual trapping in naturally water-wet and artificially tailored oil-wet limestones: Implications for geological CO_2 storage

Johny Mouallem[1]*, Ridha Al-Abdrabalnabi[2], Arshad Raza[3], Mohamed Mahmoud[3], Abubakar Isah[4], Muhammad Arif[1]*

[1]*Department of Chemical & Petroleum Engineering, Khalifa University, Abu Dhabi 127788, United Arab Emirates*

[2]*Center for Integrative Petroleum Research, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*

[3]*Department of Petroleum Engineering, College of Petroleum Engineering & Geosciences, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

[4]*Harold Vance Department of Petroleum Engineering, Texas A&M University, College Station 77843, United States*

Keywords:
Residual trapping
carbon dioxide
geological storage
wettability
trapping efficiency

Cited as:
Mouallem, J., Al-Abdrabalnabi, R., Raza, A., Mahmoud, M., Isah, A., Arif, M. Experimental investigation of CO_2 residual trapping in naturally water-wet and artificially tailored oil-wet limestones: Implications for geological CO_2 storage. Advances in Geo-Energy Research, 2025, 17(1): 43-55.
https://doi.org/10.46690/ager.2025.07.04

Abstract:
The wetting behavior of rock/CO_2/brine systems highly impacts the fluid distribution at the pore-scale and multiphase flow at the macroscale and is considered a key parameter controlling the CO_2 residual trapping in geological storage. The effect of wettability on residual trapping is, however, still uncertain as the current literature suggests high discrepancies among the published datasets. Moreover, the dataset for residual trapping observations for non water-wet carbonate rocks is relatively scarce; none of the published studies investigated this aspect in CO_2-wet limestones. Thus, a series of core-flooding experiments was conducted at reservoir conditions for three limestone samples having different wettability states, water-wet, intermediate wet, and CO_2-wet. Wettability alteration of sister rocks was achieved using stearic acid to mimic the wettability alteration in saline aquifers due to the interaction with natural organic compounds. Notably, increasing the hydrophobicity of limestone tends to decrease CO_2 residual trapping efficiency $\sim$ 19% and 37% when the initial water-wetting state shifts to intermediate-wet and CO_2-wet, respectively. This is attributed to the fluid distribution at the pore scale, in particular the wetting layers, and its effect on the CO_2/brine displacement. In case of CO_2-wet rocks, macroscopic CO_2-wetting layers act as flow paths, which reduces the residual CO_2 saturation from 29% (water-wet) to 8%. These findings advocate water-wet rocks as better candidates for CO_2 residual trapping and provide insights into residual trapping-rock wettability correlation pertinent to CO_2 geo-storage.

1. Introduction

The efforts to implement efficient solutions to counter climate change are highly desired due to the alarming increase in anthropogenic gas emissions, especially CO_2, into the atmosphere (AlDhuhoori et al., 2024). Therefore, Carbon Capture and Storage (CCS) has been recognized as one of the promising techniques to decrease the concentration of CO_2 and mitigate its harmful consequences (Krevor et al., 2023; Wang et al., 2024). The first phase of this technique is to capture the emitted CO_2 by chemical and physical processes, while the second phase is to inject it into the underground for safe and

Yandy
Scientific
Press

---

*Corresponding author.

E-mail address: 100061034@ku.ac.ae (J. Mouallem); ridhaa@kfupm.edu.sa (R. Al-Abdrabalnabi); arshad.raza@kfupm.edu.sa (A. Raza); mmahmoud@kfupm.edu.sa (M. Mahmoud); abubakar.isah@tamu.edu (A. Isah); Muhammad.arif@ku.ac.ae (M. Arif).

Received March 30, 2025; revised May 2, 2025; accepted June 10, 2025; available online June 19, 2025.

permanent storage (Mouallem et al., 2023).

CO_2 can be sequestrated in the underground through different trapping mechanisms, i.e., structural, residual, dissolution, and mineral trapping. The interplay of these trapping mechanisms results in the immobilization of the injected CO_2 and avoids its leakage to the surface (Mouallem et al., 2024). Specifically, residual trapping, also called capillary trapping, hinders the CO_2 upwards migration, ensures CO_2 entrapment into the rock pore space, and contributes towards containment security (Krevor et al., 2015). Therefore, it is crucial to further characterize this trapping mechanism and how it can be affected by physicochemical properties, including rock wettability.

Among the prospective storage sites for CO_2, e.g., depleted oil/gas reservoirs, saline aquifers, and basaltic formations, saline aquifers are considered the best candidates given their large storage capacity (Mouallem et al., 2023; Wei et al., 2023). A wide body of published papers investigated CO_2 storage in saline aquifers considering unaltered rock wettability. Nonetheless, this assumption may not always be true, given that the presence of naturally occurring organic compounds can reduce the hydrophilic characteristics of the host rock (Iglauer, 2017; Al-Shirawi et al., 2021; Baban et al., 2021, 2022). Indeed, organic acids play an important role in this matter as they tend to drastically increase the contact angle of the corresponding geo-system.

Upon CO_2 injection into the storage site, and due to gravity forces, the supercritical gas starts to migrate upwards, as a continuous phase, forming a CO_2 plume, displacing the native brine. However, at the plume tail, and because of capillary forces, the water imbibes back into the invaded CO_2 pores, disconnecting the CO_2 continuous phase, resulting in CO_2 ganglions. This trapping mechanism is a key process in maximizing containment security as the residually trapped CO_2 is immobile. At the core scale, and after conducting a typical cycle of core-flooding experiments, the initial gas saturation (S_{gi}) is obtained after the drainage process, while the residual gas saturation (S_{gr}), quantifying the residual trapping mechanism, can be obtained after the imbibition phase. As a final step, trapping efficiency (R) is calculated as the ratio of S_{gr} to S_{gi} (Bachu et al., 2013). Additionally, the relationship between these two saturations is called the characteristic trapping curve, and it has been modeled through different widely applied empirical models such as Land and Spiteri models.

In relation to multiphase flow in porous media, CO_2 injection represents the drainage process in which the non-wetting fluid is displacing the wetting fluid, in the case of water-wet rocks (Rezk et al., 2024). Conversely, the water invasion of CO_2-saturated pore space represents the imbibition process (Krevor et al., 2015). However, wettability change can reconfigure the fluid distribution at the pore scale and highly influence the multiphase flow (Andrew et al., 2014; Krevor et al., 2015; Al-Menhali et al., 2016; Rasmusson et al., 2018). Consequently, the residual trapping mechanism is highly affected by the initial wettability of the host rock (Burnside et al., 2014; Purswani et al., 2024).

In this context, several authors previously investigated the impact of wettability on the CO_2 residual trapping mechanism (Table 1). Chaudhary et al. (2013) observations indicated that residual trapping is enhanced in water-wet porous media. Similarly, Rahman et al. (2016) reported that residual trapping is more pronounced in water-wet sandstone rocks. Another investigation (Al-Menhali et al., 2016) conducted core-flooding experiments on water-wet and mixed-wet rocks, and the findings advocated that trapping efficiency decreases when wettability shifts from water-wet to mixed-wet, with an increase in Land trapping coefficient. Also, a series of studies (Baban et al., 2021, 2022, 2023a, 2023b) suggested, using core-flooding experiments performed coupled with Nuclear Magnetic Resonance (NMR) investigation, that CO_2 residual trapping efficiency decreases when contact angle increases with less rock hydrophilic characteristics. On the contrary, Hu et al. (2017) do not support this finding and reported that an additional 15% of residual CO_2 saturation was observed for the less water wetting geo-system due to bypass trapping. Likewise, Teng et al. (2022) advocate that the stronger the water-wet characteristics, the lower the residual CO_2 saturation. Recently, Lawal et al. (2024) conducted core-flooding experiments on two sandstone samples with different wettability, and it was found that the oil-wet sample exhibits higher residual trapping capacity than the water-wet sample.

Thus, the effect of wettability on residual trapping is still uncertain, as two schools of thought exist. The first group suggests that CO_2 residual trapping decreases when wettability shifts towards CO_2-wet. The authors related this decrease to the more pronounced CO_2/brine displacement occurring in the porous media when wettability is altered, which significantly reduces residual CO_2 saturation. When wettability is shifting towards CO_2-wet, it is believed that brine displaces CO_2 from large pore bodies, which significantly reduces CO_2 saturation, and traps it in the narrowest and smallest areas. Consequently, the cluster size of the trapped CO_2 in the porous media was found to be smaller in CO_2-wet rocks, which further reduces CO_2 saturation. One more factor contributing to less residual CO_2 saturation was the low mobility ratio (viscosity of CO_2 over viscosity of brine), which endorses stable front displacement rather than viscous fingering, thus displacement of CO_2 is further facilitated. However, this aspect requires more investigation as the injection rate plays an important role in determining the flow regime. More importantly, the formation of thin wetting layers, consisting of CO_2, creates a pathway for the non-polar fluids in the CO_2-wet rocks scenario. CO_2-wetting layers acting as flow streams facilitate the displacement of CO_2 with the continuous brine injection into the porous media. This is believed to be the most dominant physicochemical phenomena leading to less residual CO_2 saturation.

On the other hand, the second group believes that CO_2-wet rocks enhance the residual trapping of CO_2 due to: 1) cooperative pore filling, and 2) CO_2/rock interactions. It was concluded that smaller contact angles improve the cooperative pore filling, thus less bypass of the defending fluid (CO_2), which results in less trapped CO_2. In higher contact angle systems, the brine flow channels are relatively wider, with a lower displacement front velocity, which enhances the bypass

Table 1. Literature showing the wettability effect on CO_2 residual trapping.

Reference	Lithology	K (mD)	ϕ (%)	Wettability	S_{gi}	S_{gr}	R	C^*
Chaudhary et al. (2013)	Glass bead	/	37	Water-wet	24	15	62.5	2.5
	Glass grain pack	/	33	Water-wet	22	20	90.91	0.45
	Teflon packs	/	39	CO_2-wet	25	2	8	46
Rahman et al. (2016)	Sandstone	1,800	22	Water-wet	50.6	14.9	29.45	4.74
				CO_2-wet	49.2	8.7	17.58	9.46
Al-Menhali et al. (2016)	Carbonate	138	28	Water-wet	30.36	20.26	66.71	1.64
					20.59	13.19	64.05	2.72
					29.11	19.61	67.38	1.66
		148	29	Mixed-wet	39.22	15.17	38.67	4.04
					37.39	14.11	37.75	4.41
					19.52	11.62	59.52	3.48
Hu et al. (2017)	Micromodel	/	24	Water-wet	/	27	/	/
				Intermediate wet	/	41.5	/	/
Iglauer et al. (2019)	Sandstone	2,047	21	Oil-wet	41	13.5	32.62	4.97
Baban et al. (2021)	Sandstone	35	21	Water-wet	31	23	74.19	1.12
					20.03	7.04	35.13	9.21
					23.12	14.51	62.77	2.57
					37.86	12.5	33.01	5.36
					46.83	20.76	44.32	2.68
					55.69	18.94	34	3.48
Baban et al. (2022)	Sandstone	35	21	CO_2-wet	52	12	23	6.41
Baban et al. (2023a)	Dolomite	65	11	Water-wet	29	18	62.07	2.11
				CO_2-wet	28	14	50	3.57
Baban et al. (2023b)	Sandstone	35	21	Water-wet	44	20	45.45	2.73
				CO_2-wet	37	12	32.43	5.63
Teng et al. (2022)	Sandstone	834	24	Water-wet	60.1	19.06	31.72	3.58
					71.3	20.19	28.32	3.55
					76.74	20.19	26.31	3.65
				Intermediate-wet	60.7	18.2	30	3.85
					57.33	17.63	30.75	3.93
Lawal et al. (2024)	Sandstone	/	22	Water-wet	55.2	18.1	32.78	3.71
				CO_2-wet	73.22	31.9	43.5	1.77
This study	Limestone	17.6	27	Water-wet	65	29	45	1.9
		18.8	30	Intermediate-wet	72	19	26	3.8
		18.8	26	CO_2-wet	88	8	9	11.3

* It is noteworthy that the Land coefficient, C, was not reported in most of the studies, thus the calculated value of C is listed here.

Table 2. Routine core analysis and wettability characterization.

Sample	Diameter (mm)	Length (mm)	ϕ (%)	K (mD)	Initial wettability	Contact angle (°)	Final wettability
D1	38.46	76.5	17.67	27.29	Water-wet	60	Water-wet
D2	38.55	76.5	18.80	30.6	Water-wet	93	Intermediate-wet
D3	38.41	76.5	19.76	26.1	Water-wet	123	CO_2-wet

trapping, thus greater residual trapping. Furthermore, authors advocate that CO_2 will adhere to the rock surface as the affinity of CO_2 towards the rock surface is more pronounced in oil-wet reservoirs rather than water-wet reservoirs. CO_2/rock interactions, during drainage and imbibition processes, highly affect the surface chemistry of the rock, which promotes CO_2 adsorption. Consequently, the residual CO_2 saturation increases as more CO_2 is adsorbed into the rock surfaces in oil-wet reservoirs.

In light of the above, it is evident that the current data suggests complexity and ambiguity in terms of a clear correlation between wettability and residual trapping efficiency, i.e., for water-wet vs. CO_2-wet systems. In this study, we aim to limit this discrepancy and provide a trend/correlation that clarifies the relationship between residual trapping efficiency and rock initial wettability. Additionally, it can be noticed that 1) the intermediate-wet systems are rarely investigated (Table 1), and 2) while carbonates are infrequently analyzed, limestones still lack data on residual trapping under variable wettability conditions. Due to the higher heterogeneity and complexity of pore structure and geometry in carbonates compared to sandstones, it is crucial to conduct core-flooding experiments in carbonate samples to investigate CO_2 residual trapping as a function of rock wettability state. Core flooding experiments are conducted at the core scale rather than the pore scale to include several geological complexities that are highly relevant to the residual trapping mechanism. Spurin et al. (2025) suggested that more fluid pathways are involved at the core scale, and experiments at the pore scale may not truly represent the subsurface conditions with the relevant fluid flow dynamics. Furthermore, several phenomena such as relaxation of fluids after experiments, CO_2 dissolution in brine, and flow regimes (viscous/capillary) are highly affected by larger experimental scale. Therefore, the novelty of this study covers the investigation of the residual trapping capacity of limestone samples of water-wet, intermediate-wet, and CO_2-wet characteristics. The workflow comprises: 1) preparation and characterization of the core samples to ensure that they share the same mineralogical and petrophysical properties, 2) artificial wettability alteration towards intermediate-wet and CO_2-wet states using stearic acid, and 3) core-flooding experiments to quantify and analyze the trapping efficiency in each wettability state. In addition to that, the presence of naturally occurring organic acids is considered in this study, which tends to result in a wettability regime transition from a water-wet state to a more non-wetting state. This approach differs from the previous studies investigating the residual trapping in carbonates, in which wettability transition was achieved using silane and crude oil, which are highly relevant to enhanced oil recovery applications. The core flooding experiments are conducted at reservoir conditions to mimic the real conditions of CO_2 storage applications and consist of drainage and imbibition processes. Initial gas saturation and residual gas saturation are measured for each system to reflect on the CO_2/brine displacement and the physicochemical processes leading to those values. Later, a systematic analysis is accomplished on how wettability changes in the saline aquifer can alter the residual trapping characteristics of CO_2. The findings of this work contribute to providing better knowledge and understanding of residual trapping in CO_2 geo-storage applications and how it can change with rock wettability.

2. Methodology

2.1 Samples and fluids preparation

The core-flooding experiments are conducted on Indiana limestone core samples, formed in a shallow inland sea depositional environment during the Mississippian period, with a mineralogical composition of 99.7% calcite and 0.3% quartz as per X-ray Diffraction (XRD) analysis. XRD results validate the similarity in the mineralogical composition of the three samples that consist mainly of calcite with an insignificant presence of quartz (SiO_2) and the absence of any other secondary mineral like dolomite $CaMg(CO_3)_2$. More information about the pore types of Indiana limestone formation having a similar range of permeability can be found in Mouallem et al. (2025). The samples share the same petrophysical properties (porosity and permeability) and are saturated with the same brine solution having a salinity of 21.4 wt%. The brine is synthetically prepared, consisting of several bivalent and monovalent salts (NaCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, $NaHCO_3$) mixed with pure deionized water (DI) to mimic the composition of the real formation brine found in the Arab-D reservoir (Mouallem et al., 2024) to ensure representative characterization of the rock/fluids and fluid/fluid interactions, including wettability. Pure carbon dioxide (purity $> 99\%$) is used in the experiments. Additionally, pure nitrogen gas and toluene are used for cleaning purposes. For wettability alteration purposes, the carbonate samples were saturated with a chemical solution comprising stearic acid ($CH_3(CH_2)_{16}CO_2H$) and n-decane ($C_{10}H_{22}$) as model oil (Isah et al., 2023). The process is discussed in the subsequent section. Notably, the three limestone samples exhibit the same initial wettability state at experimental conditions ($P = 10$ MPa and $T = 323$ K) (Table 2). Given that wettability is not dependent on porosity

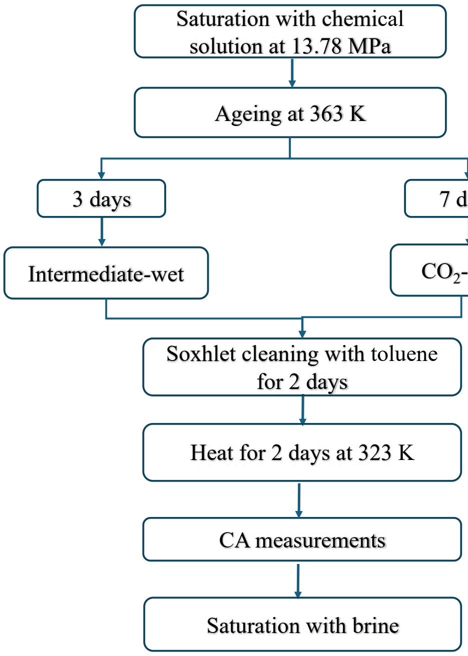

Fig. 1. Wettability alteration workflow.

or permeability, the only difference among the three samples is the wetting state after implementing the wettability alteration process.

2.2 Wettability alteration

The objective of this section is to replicate the subsurface conditions for the core-flooding experiments. As the focus is on wettability effects on residual trapping, the sample wettability must be artificially altered towards two scenarios: intermediate-wet and CO_2-wet saline aquifer.

Carbonate geological formations are associated with the highest heterogeneity among the different lithologies and can exhibit different wetting states. Although the saline aquifer is normally saturated with formation brine and a water-wet state is expected, wettability can be altered due to the presence of naturally occurring organic acids that reduce the hydrophilic nature of the rock and render aquifers less water-wet (Al-Shirawi et al., 2021; Ali et al., 2022; Baban et al., 2023a). These organic compounds result from geological events (Iglauer et al., 2014). Several studies investigated the effect of organic acids, i.e., stearic acid, lauric acid and oleic acid on wettability of calcite/CO_2/brine systems and it was found that indeed these acids tend to increase the contact angle, thus a shift towards intermediate wet state or even CO_2-wet state occurs (Ali et al., 2021). Practical applications in the laboratory were applied successfully to alter the initially water-wet calcite samples to less water-wet states (Al-Shirawi et al., 2021; Baban et al., 2022; Arain et al., 2023; Lawal et al., 2024).

As described above, the samples share the same mineralogical and petrophysical properties as well as the initial brine solution. To change the wettability of D2 and D3 to intermediate and CO_2-wet state, respectively, a delicate chemical process was applied (Fig. 1). The first step was to prepare the chemical solution for the core sample saturation. 0.013 M of stearic acid was dissolved in 1 L of n-decane model oil - consistent with previous applications. Note that 0.01 M of stearic acid represents the optimal concentration for the highest adsorption rates of stearate molecules on calcite surfaces. In fact, a few authors measured the concentration of organic acids in subsurface water, and they reported values ranging between 0.007 and 0.017 M (Lundegard and Kharaka, 1994). Interestingly, they correlated organic acid concentration with time, temperature, and depth. Several researchers investigated the effect of organic acid concentration on the wettability alteration process. They conducted contact angle measurements on treated quartz/calcite samples using different acid concentrations and types to examine the optimal acid concentration that should be used for the organic acid treatment experimental procedure. The results suggested that increasing acid concentration leads to higher contact angles, thus less water-wet characteristics. Moreover, this trend is similar for the four organic acids examined. Therefore, with higher acid concentration, higher contact values can be achieved. Nevertheless, it must be noted here that a concentration of 0.01 mol/L is sufficient to reach high contact angle values and shift the wettability towards the CO_2-wet state. Later, samples D2, D3, and their sister samples (D2' and D3') were vacuumed for 12 hours, then saturated with the chemical solution at 13.78 MPa for a full day to ensure the full invasion of the pore system. Step 2 consists of ageing the samples at a temperature of 343 K for a duration of 3 days for D2 and D2' to reach the intermediate wet state, and 7 days for D3 and D3' to reach the CO_2-wet state. Once the ageing phase was completed, the samples were cleaned for 2 full days using the Soxhlet process with toluene to remove the n-decane phase, then placed in the oven at a temperature of 323 K to dry up the toluene. The n-decane solution was only used as a model oil to facilitate the adsorption of stearic acid molecules on sample surfaces. Therefore, the scope of work of this study is related to saline aquifers with two phases and not to oil/gas reservoirs comprising three phases. Finally, the sacrificial samples (D2' and D3') were dry cut, and flushed with pure nitrogen to detach the excess stearic acid in order to conduct contact angle measurements as explained below. Once the process is successful and the contact angle has increased, samples D2 and D3 were saturated with brine to initiate core-flooding experiments.

2.3 Wettability measurements

The sessile drop method is shown to be an efficient and widely used technique to measure the contact angle of rock/CO_2/brine systems (Mutailipu et al., 2019). This method consists of dropping a brine droplet on the rock substrate surrounded by the CO_2 phase (Stevar et al., 2019). A series of contact angle measurements were performed on the samples before treatment, and on D2' and D3' after treatment to ensure the success of the wettability alteration process described above. A further assessment of limestone/CO_2/brine wettability is provided in this study; thus, contact angle experiments were conducted on the three samples at pressures ranging from 0.1 to 14 MPa and at two temperatures of 298 and 323 K.

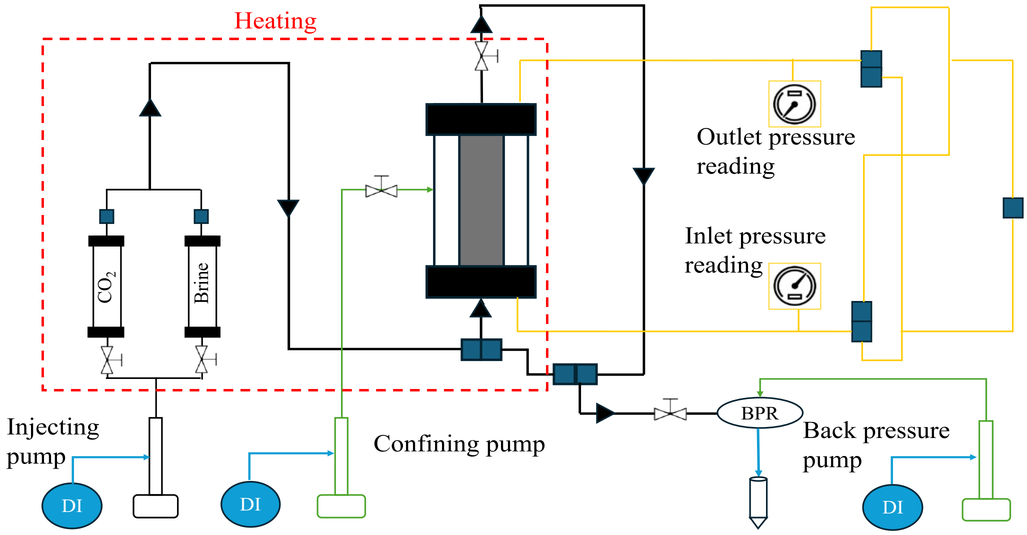

Fig. 2. Experimental set-up diagram showing the different pumps, core holder, accumulators, valves, pressure gauges, and the heating system (after Mouallem et al. (2025)).

Table 3. Density, viscosity, and IFT of CO_2 and brine at the experimental conditions.

Fluid	Density (kg/m^3)	Viscosity (cP)	IFT (mN/m)
Formation brine	1,130	0.65	39.16
CO_2	396	0.028	39.16

2.4 Experimental setup and procedure

A series of core-flooding experiments are carried out using advanced automated high-pressure high-temperature equipment (LXRS-300) illustrated in Fig. 2. The details of the system can be found in Appendix A and in a recent study (Mouallem et al., 2025).

The experimental conditions ($P = 10$ MPa and $T = 323$ K) mimic the actual conditions of subsurface geological features and the supercritical conditions of CO_2 during CCS applications. Moreover, the overburden pressure was selected as 13.8 MPa to ensure CO_2 will flow into the core sample, and the pore pressure (back pressure) is equal to 10 MPa. The fluid characteristics under these conditions are presented in Table 3.

A total of three cycles of experiments are performed in this study, comprising two phases: 1) primary drainage, in which CO_2 is injected into the fully brine-saturated core, and 2) secondary imbibition, in which brine solution is injected into the core saturated with CO_2 and brine. In the drainage phase, the injected sc-CO_2 will displace the native brine and saturate the core. Therefore, this experiment was stopped until no brine was further discharged from the core. On the other hand, in the imbibition phase, the injected brine would displace out CO_2 and brine. Thus, this experiment is stopped when a continuous flow of brine is collected in the beaker with no trace of CO_2. A total of eight Pore Volumes (PVs) of CO_2 and brine were injected in the drainage and imbibition phases, respectively. By following this sequence, the initial gas saturation (S_{gi}) and the residual gas saturation (S_{gr}) can be obtained from drainage and imbibition, respectively using the mass balance approach. Subsequently, the residual trapping efficiency was calculated as a ratio of S_{gr} over S_{gi}. Both drainage and imbibition processes are achieved at an injection rate of 0.5 cc/min to ensure that the flow regime is dominated by capillary forces that enhance the residual trapping of CO_2. A recent study by Mouallem et al. (2025) investigated the injection rate effect on CO_2 saturation by increasing the injection rate from 0.5 cc/min to 1 cc/min, then finally to 2 cc/min. The results indicated that increasing the CO_2 injection rate leads to higher initial CO_2 saturation in the drainage process. More importantly, the capillary fingering flow regime remains the dominant displacement mechanism at 2 cc/min. A further increase in flow rate may lead to the shift of the flow regime towards stable front displacement, which is beyond the scope of this study. However, for the imbibition process, a constant flow rate of 0.5 cc/min is selected to represent the stable water imbibition flow rate during experiment, which is also controlled by capillary-dominated displacement. Note that in an actual CO_2 storage project, once CO_2 injection is stopped, brine naturally imbibes back to reoccupy the pore space.

It is noteworthy that the margin of error associated with this core-flooding equipment is highly dependent on the operating parameters, e.g., pressure, temperature, and flow rate. Therefore, the experiments were carried out with constant pressure monitoring and flow rate control to limit the uncertainties and obtain accurate results. These variables can significantly affect the fluid properties, e.g., density, the CO_2/brine displacement, and the initial and residual CO_2 saturations.

Furthermore, the collected brine is measured visually in the beaker to get its volume and weighed using a high accuracy weighing balance to obtain the weight for mass balance cal-

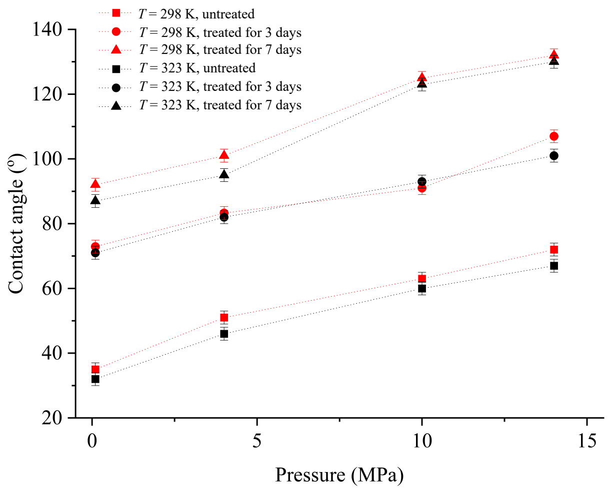

Fig. 3. Indiana limestone/CO_2/brine contact angle of D1', D2', and D3' at different pressures and temperatures.

culations. In addition, the initial and residual gas saturations are highly dependent on the core characterization phase i.e., porosity, saturation, and pore volume. For this reason, special attention was given to this critical phase to ensure correct petrophysical properties essential in the calculation of S_{gi} and S_{gr}. Any slight deviation in these parameters leads to significant errors in the initial and residual CO_2 saturations.

3. Results and discussion

This section is mainly divided into two subdivisions, examining the degree of success of the wettability alteration process and investigating the trapping efficiency of each sample having a different wettability state.

3.1 Wettability alteration

The aim of this section is to ensure that samples D2 and D3 exhibit the wettability state needed for this study. Two different methods were used to confirm the wettability alteration: 1) contact angle measurements at high pressure and temperature before and after treatment, and 2) Scanning Electron Microscopy (SEM) imaging analysis to prove the surface mineralogical change after treatment.

3.1.1 Contact angle

Wettability change was assessed through contact angle measurements of the untreated and the treated (for 3 and 7 days, respectively) samples. To have a better understanding of the wettability phenomena, contact angle measurements were conducted as a function of pressure and temperature for the three different samples, and a new data set was generated. Although several studies investigated extensively the wetting behavior of the calcite/CO_2/brine systems, as presented in the recent review. However, this study examines the wettability change of altered calcite/CO_2/brine systems when pressure and temperature change. Fig. 3 displays the contact angle variation with pressure increase at two temperatures for the treated and untreated samples. Contact angles tend to increase monotonically with increasing pressure (Fig. 3) due to the density increase of CO_2 with pressure. However, temperature tends to decrease the contact angle slightly (by 2-3°) as the curves slightly shift downwards. Interestingly, the same pattern is detected for all tested samples, which implies that the presence of organic acids does not lead to any changes in the well-established relationship between contact angle and its influencing factors (temperature and pressure). These findings are also highly consistent with the literature (Isah et al., 2023).

On the other hand, the contact angle measurements reveal that untreated samples (D1, D2, D2', D3, D3') are strongly water-wet before treatment. For instance, the contact angle at ambient conditions for the untreated sample records 32° and increases up to 59° at experimental conditions, which is still in the water-wet range. However, the contact angles display a notable increase after three days of ageing with stearic acid to reach 93° at the experimental conditions (10 MPa and 323 K). Finally, ageing for 7 days with the formulated chemical solution leads to a CO_2-wet state as the contact angles exhibit a massive increase to values greater than 110o at the selected experimental conditions. In summary, we can clearly state that the wettability shifted to intermediate-wet and CO_2-wet after implementing the chemical treatment.

Mineral composition is also a crucial factor to consider in this section. While the core samples consist mainly of calcite (99.7%), real carbonate saline aquifers may slightly differ in their mineralogy. Mineralogical heterogeneity may include clay or silica impurities that can affect the intrinsic wettability of the system. It is believed that silica tends to remain water-wet at operating conditions, while the presence of clay tends to increase the contact angle at the same operating conditions (Ali et al., 2023). Therefore, accurate mineralogical composition is essential for the reservoir characterization prior CO_2 injection.

3.1.2 Mineralogical composition

Another approach to confirm the wettability alteration was to investigate the rock surface morphology before and after the treatment. Mechanistically, the stearate ions of the stearic acid will adsorb to the rock surface, changing the surface chemistry and ultimately wettability. Adsorption of stearate ions to the calcite surface is the main mechanism leading to wettability alteration. In fact, these ions are byproducts of the dissociation reaction of stearic acid molecules as expressed below (Al-Shirawi et al., 2021):

$$CH_3(CH_2)_{16}COOH = H^+ + CH_3(CH_2)_{16}COO^- \tag{1}$$

The negatively charged ions react mainly with Ca^{2+} present at the limestone surface, by ion exchange mechanism, and form calcite stearate compounds. Consequently, zeta potential records negative values, thus wettability is changed. To visualize the stearic acid adsorption, the SEM imaging technique was used. Fig. 4 depicts the micrographs of the untreated and treated rock samples with stearic acid solution. The images show that after treatment, the rock surface presents layers/deposits of the stearate molecules adsorbed. The latter is more pronounced and abundant in the seven-day aged sample. Therefore, the adsorption of stearic acid is confirmed with no changes in rock morphology as seen in the SEM images at 20 μm.

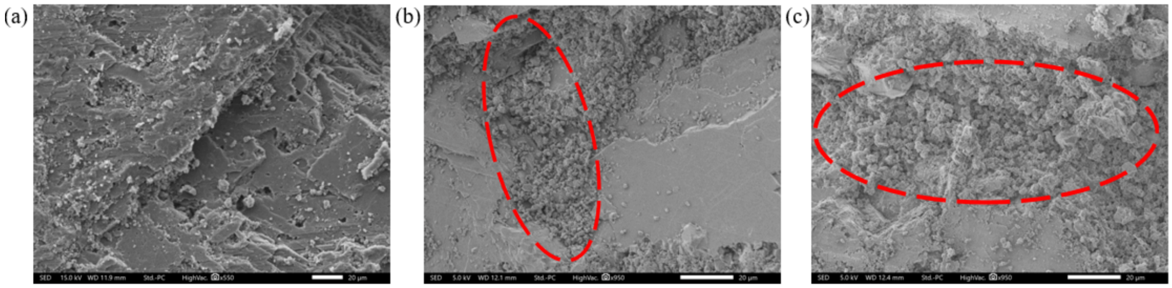

Fig. 4. SEM images showing the core sample surfaces: (a) Before, (b) after 3 days of treatment, and (c) after 7 days of treatment..

Table 4. EDXS results of the initial and untreated samples.

Element	Initial (wt%)	3 days of ageing (wt%)	7 days of ageing (wt%)
Ca	37.92	33.93	27.57
C	15.00	17.56	19.08
O	47.08	48.51	53.35

Table 5. Initial gas saturation and brine produced for the three different samples.

Sample	Wettability	Effective PV	Brine displaced (cc)	S_{gi}
D1	Water-wet	12.49	7.2	0.65
D2	Intermediate-wet	11.68	8.4	0.72
D3	CO_2-wet	9.67	8.5	0.88

Furthermore, the elemental composition of the samples was measured using Energy-Dispersive X-Ray Spectroscopy (EDXS). The latter reveals the changes in mineralogical composition after stearic acid treatment. The initial elemental composition of the fresh limestone sample was measured, followed by the elemental composition of the sample treated for three days, and finally the seven-day treated samples. The results presented in Table 4 indicate that after treatment, the weight percentages of carbon and oxygen are increasing, while the mass composition of calcium is decreasing. This is expected as stearic acid is mainly composed of carbon and oxygen elements. The increase of these two elements further confirms the stearic acid adsorption, leading to wettability alteration. Moreover, it can be noticed that the change in the elemental composition is more pronounced after seven days of treatment, which indicates higher adsorption of stearate ions to the limestone surface. For instance, the mass percentage of carbon increases from 15% to 17.56% after three days of ageing, while it reaches 19.08% after seven days. Oxygen mass composition changes also follow the same pattern. However, calcium weight percentage is decreasing from 37.92% to 33.93% after three days of treatment, while it decreases furthermore to 27.47% after seven days.

3.2 Core-flooding experiments

This section presents the results of the core-flooding experiments conducted on the three samples with different wettability states to investigate how residual trapping efficiency can be affected by the rock initial wetting state.

3.2.1 Drainage

Initial gas saturation and residual gas saturation are obtained experimentally after the drainage and imbibition processes, respectively. In the drainage phase, S_{gi} is recorded after injecting a sufficient PVs, at a rate of 0.5 cc/min, to reach stabilization in pressure profile (i.e., a constant pressure drops), and constant cumulative brine production (i.e., no further discharge of brine).

Table 5 presents the experimental results of the drainage phase, showing the initial CO_2 saturation and brine produced for the three samples (D1, D2, and D3) with different initial wetting states. It is noteworthy that by initial state, we mean the initial wettability state prior to core-flooding experiments and after wettability alteration for D2 and D3. It can be clearly seen that wettability has a significant effect on the initial gas saturation and multiphase flow in CO_2 storage application at the core scale. It can be detected that S_{gi} is increasing when rock shifts from the water-wet state to the intermediate and CO_2-wet state. For instance, S_{gi} increases from 65% to 72% in the intermediate-wet rock sample, while it further increases to 88% when the rock exhibits a CO_2-wet state. Higher CO_2 saturation after the drainage phase indicates higher brine displacement from the core, which can be detected as well in the brine produced from each sample. This notable brine displacement is highly attributed to the change in the capillary pressure curve. The latter tends to shift downwards and to the left when wettability changes from water-wet to CO_2-wet (Mirzaei-Paiaman and Okuno, 2024). As a result of this, gas invasion is more facilitated when the rock is exhibiting less hydrophilic, thus higher brine displacement. In addition to that, the significant increase in S_{gi} is related to the change in relative permeability curves (Al-Khdheeawi et al., 2017). Studies indicate that increasing CO_2/brine/rock contact angle leads to the reduction of CO_2 relative permeability and an increase in water permeability (Juanes et al., 2006; Mirzaei-Paiaman and Okuno, 2024). Therefore, altering the wettability state towards more CO_2-wet would lead to more brine displ-

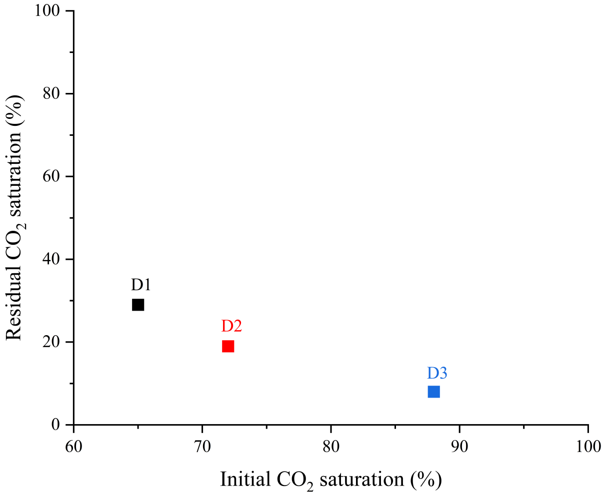

Fig. 5. Residual gas saturation versus initial gas saturation of the three samples.

acement at the core scale (Gao et al., 2025).

Additionally, at the pore scale, wettability alteration of the rock sample results in fluid distribution reconfiguration in the porous media. In fact, in water-wet rocks, water will occupy the small areas in the pore space as well as coat the rock surface to form a thin water film called wetting layers. However, in CO_2-wet rocks, when the two phases (water and CO_2) co-exist in the pore space, CO_2 tends to coat the rock surfaces and form CO_2 wetting layers, while water will be occupying the larger areas. Consequently, more water is exposed to being displaced by the continuous injection of CO_2 into the porous media, thus more water is displaced after drainage. In other words, after the formation of CO_2 wetting layers, the water phase in the porous media is prone to be displaced, which is reflected in higher brine production, thus higher S_{gi}.

3.2.2 Imbibition

After completing the drainage process, imbibition takes place under the same operational conditions to obtain residual CO_2 saturation. S_{gr} is recorded in the imbibition phase after injecting the needed brine PVs, at a rate of 0.5 cc/min, to ensure that no further gas is being displaced out of the core. The injected water invades the porous media and displaces some of the CO_2 saturating the pore spaces, leaving behind residual CO_2 in the pore spaces. The relationship between S_{gi} and S_{gr} is a crucial parameter in the quantification of residual trapping. Fig. 5 displays the residual CO_2 saturation, obtained after imbibition, as a function of the initial CO_2 saturation obtained after drainage for each sample. It can be clearly observed that residual CO_2 saturation is decreasing with the change of the initial wettability state of the rock. For example, residual gas saturation decreases from 29% to 19% when the wettability shifts from water-wet state to intermediate-wet state. The same pattern is detected for D3, which is more CO_2-wet than D2. A further decrease in residual gas saturation occurs, and S_{gr} drops down to 8% when the rock sample is CO_2-wet. These findings indicate that wettability alteration drastically changes the CO_2 residual saturation. Therefore, the results imply that snap-off mechanism responsible for disconnecting the CO_2 continuous phase is less pronounced in CO_2-wet rocks. This significant decrease in S_{gr} is highly attributed to the fluid distribution at the pore scale. Particularly, in CO_2-wet rocks, CO_2 is coating the surfaces, which means that the concept of wetting layer swelling is not applicable anymore in pore spaces and throats. The injected water will displace the CO_2 accumulated in the pore space, not the CO_2 adhered to the surface. Thus, at the pore throat, water is not contributing to a notable disconnection of the CO_2 phase, as is the case in water-wet rocks, which highly influences the snap-off mechanism. Additionally, given the fact that water is more viscous than CO_2, higher displacement efficiency has resulted, which also contributes to lower residual trapping. Subsequently, only a minimal volume of CO_2 is being residually trapped in the pore space, while most of the remaining CO_2 in the porous media is coating the surfaces, which is much less in volume compared to ganglions. Furthermore, CO_2 has a higher affinity to CO_2-wet rocks rather than water-wet rocks, thus microscopic CO_2 layers are formed on the rock surfaces, which provide flow conduits for CO_2 that enhance the flow connectivity of CO_2 in the porous system. Also, these layers are interconnected and located in the small areas of the pore body, which makes it difficult to break by water imbibition (Baban et al., 2021, 2023b). This phenomenon is competing with the snap-off mechanism occurring in water-wet rocks, where water disconnects the continuous phase of CO_2 located in the central areas of the pores. Consequently, during imbibition, CO_2 flows through these thin films, and a notable saturation decrease is observed. Therefore, the snap-off mechanism is less pronounced in this type of fluid configuration.

3.2.3 Trapping efficiency

An analogous trend is observed for the residual trapping efficiency. The latter decreases significantly when wettability alters from water-wet to CO_2-wet, i.e., the contact angle of limestone/CO_2/brine is increasing. Fig. 6 demonstrates the relationship between the trapping efficiency, calculated as the ratio of S_{gr} over S_{gi}, and the contact angle of the different samples used in this study. It is evident that trapping efficiency is decreasing monotonously with the increase of contact angle. For instance, for water-wet rocks ($\theta = 60°$), trapping efficiency records a value of 45%, while for intermediate-wet rocks with a higher contact angle ($\theta = 93°$), trapping efficiency R decreases to 26%. Furthermore, a drastic decrease in trapping efficiency is recorded when the contact angle increases to 123o in CO_2-wet rocks. Interestingly, as observed in Fig. 5, S_{gi} is relatively higher when wettability is altered, but trapping efficiency is reduced as S_{gr} is low. This observation contradicts Land's trapping model (Land, 1969) that suggests an increase in S_{gr} with the increase of S_{gi}, but perfectly matches Spiteri's model (Spiteri et al., 2008) that proposes a decline in S_{gr} for high S_{gi}. This pattern is in direct link with the snap-off mechanism that is being highly disfavored when the contact angle increases, and fluid distribution changes accordingly. Although higher initial gas saturation is recorded after drainage in altered rock samples, water injection tends to displace out CO_2 rather than disconnecting it as small ganglia

Table 6. Residual trapping characteristics for the three samples.

Sample	Wettability	Contact angle (°)	S_{gi}	S_{gr}	R (%)	C
D1	Water-wet	60	0.65	0.29	45	1.9
D2	Intermediate-wet	93	0.72	0.19	26	3.8
D3	CO_2-wet	123	0.88	0.08	9	11.3

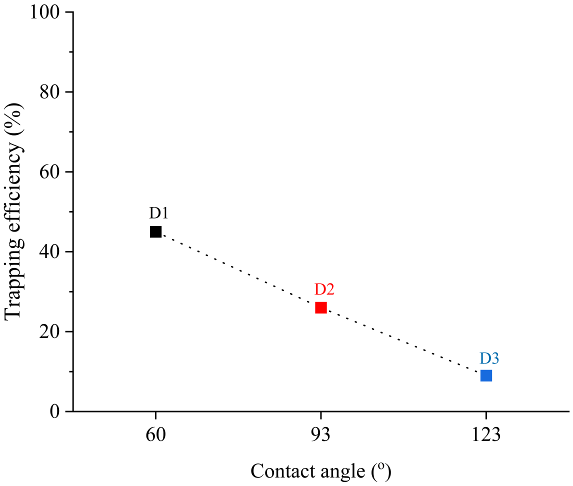

Fig. 6. Trapping efficiency versus contact angle of D1, D2 and D3.

to be trapped in the pore spaces. Additionally, at the pore scale, when wettability is shifted, water occupies the large pores while CO_2 saturates only the small areas. As a result of this, the snap-off mechanism is less favored. Mechanistically, the suitable conditions for snap-off mechanism are less favored in CO_2-wet rocks due to the following: 1) Water wetting layers swelling is not applicable, 2) water occupies the large pore bodies (center) while CO_2 occupies the corners and crevices of the pores, and 3) interconnected wetting layers consist of CO_2 which facilitates CO_2 flow as they create a flow conduit that advocates the desaturation of CO_2 Subsequently, residual trapping mechanism is less favored as CO_2 continuous phase is less disconnected when contact angle increases, thus it can be concluded that CO_2-wet rocks are considered as poor candidates for CO_2 residual trapping mechanism.

To further characterize the residual trapping mechanism of altered wettability rocks, Land's model coefficient, C, was calculated for the three different samples. As observed in Table 6, C is increasing with contact angle increasing to reach 3.8 and 11.3 for the intermediate-wet and CO_2-wet cases, respectively. The increase of C suggests less trapping of CO_2, which is clearly detected in our case as the trapping efficiency is decreasing when wettability is shifting towards CO_2-wet. However, it should be noted that C is calculated based on one point only, hence the need for additional data points to further evaluate this aspect of the trapping mechanism.

Table 6 depicts the initial gas saturation, residual gas saturation, and trapping efficiency resulting from the series of core-flooding experiments conducted in this study. Interestingly, higher initial gas saturation, S_{gi}, does not translate into higher S_{gr} as the trapping models suggest. This inversely proportional correlation is attributed to the transition of wettability towards more CO_2-wet states associated with the increase of contact angle. A 63° increase in contact angle leads to a 36% decrease in the trapping efficiency. This notable decrease advocates that water-wet saline aquifers are better candidates for CO_2 residual trapping mechanism in CCS applications. Therefore, it is well established from this study that wettability has a notable effect on the residual trapping efficiency of CO_2, which is considered a dominant trapping mechanism.

3.2.4 Comparison with literature

Data sets generated from this work are compared with the previous studies, listed in Table 1. We must note here that residual trapping is a function of several other factors e.g., lithology, rock properties, permeability, and experimental conditions. Therefore, the comparison presented in this section is not based on similar variables; our study presents, for the first time, residual trapping values for intermediate and CO_2-wet limestone rock samples. Nonetheless, the comparison contributes to better understanding of the residual trapping mechanism and how the interplay of wettability and lithology can affect S_{gi} and S_{gr}. Fig. 7 displays the S_{gr}-S_{gi} data points of the previously published papers and our data. It is well observed that the data is scattered along the S_{gi} axis ranging from 20% to 88% in the trapping characteristic graph, while it is well assembled along the S_{gr} axis ranging from 8% to 19%. This first observation indicates that S_{gr} is not recording high values in altered wettability rocks, but S_{gi} is unpredictable in this wettability state. As a second observation, our data points perfectly match with previous values of S_{gr}. However, they are deviating with respect to S_{gi} values. This can be highly attributed to the deviation in the abovementioned influencing factors, mainly lithology. In fact, this observation is expected as the same experimental conditions do not exist yet in literature, hence the need for more experimental data sets in limestone samples.

Our results conflict with previous studies that support a proportional relationship between the trapping efficiency and contact angle. The authors relate this increase in trapping efficiency when wettability is shifted towards CO_2-wet to the geochemical interactions and bypass trapping. First, Lawal et al. (2024) suggested that further CO_2 adsorption occurs in CO_2-wet rocks, which leads to higher residual gas saturation after imbibition. As a direct comparison with our work, the core-flooding experiments were performed on sandstone samples that are usually less heterogeneous than carbonate samples and comprise an entirely different mineralogy (quartz

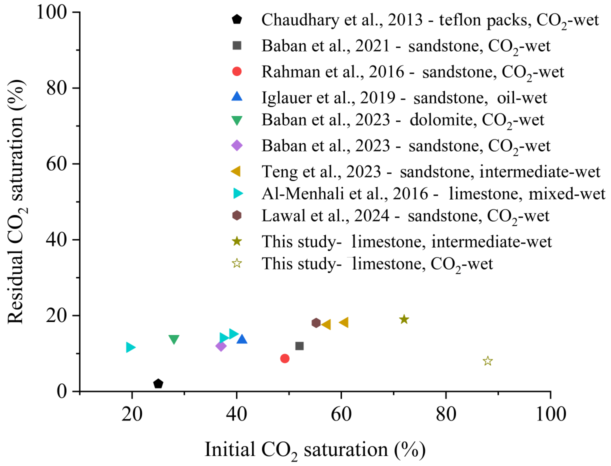

Fig. 7. Comparison of the data produced in this study with previous studies.

abundance). Moreover, Hu et al. (2017) also found an increase in residual trapping for the CO_2-wet system and related their results to the cooperative pore filling mechanism that enhances the bypass trapping, thus more residual CO_2. However, this study was carried out on a micromodel system with a different experimental procedure and saturation quantification that is not able to capture rock heterogeneity in pore structure and porous media. Therefore, these differences in lithology and experimental set-up may give rise to discrepancies with core flooding observations. Third, Teng et al. (2022) advocate for an increase in CO_2 residual saturation after imbibition due to the increase in non-wetting phase fluidity. However, the contact angle values in this study do not exceed 74.5°, they are relatively much less than the contact angle values used in our study, thus the wettability state is not shifting towards CO_2-wet but rather remains in weakly water-wet or intermediate-wet.

4. Application and limitations

The results obtained from this study at the core scale suggest that wettability alteration due to the presence of stearic acid leads to a decrease in the residual trapping capacity of CO_2. Interestingly, CO_2-wet rocks exhibit high CO_2 saturation post CO_2 injection, however, this does not lead to higher residual CO_2 saturation. In the CO_2-wet state, higher mobility of CO_2 is detected with higher displacement efficiency when water is injected. The findings indicate that residual trapping is less favored in CO_2-wet rocks due to the fluid distribution and configuration at the pore scale. Nevertheless, at the field scale, our key findings match with previous studies stating that plume migration is more pronounced in CO_2-wet rocks, wherein CO_2 migrates higher vertical distances from the injection point, than in water-wet rocks, i.e., plume thickness is larger. (Al-Khdheeawi et al., 2017). As a result of this, CO_2 plume movement is less hindered by residual trapping in CO_2-wet rocks, thus injected CO_2 reaches the seal faster where pressure is exerted by the accumulated gas underneath and might lead to leakage unless favorable subsurface conditions exist. Therefore, wettability alteration of the host rock has direct implications on the fluid distribution at the pore scale that can lead to significant effects on the residual trapping mechanism at the core scale and eventually influence the CO_2 plume movement and trapping capacities at large scale CCS operations due to changes in key petrophysical parameters e.g., capillary pressure and relative permeability curves. In light of this, accurate characterization of the reservoir is very crucial for CO_2 geo-storage applications to select suitable formations exhibiting strongly water-wet characteristics.

Major experimental challenges in this work were encountered in the wettability alteration process and in data modeling using trapping models. Most importantly, wettability alteration was evaluated on core sample slices. The contact angle was measured for each slice of the sample, and it was found that the variation does not exceed 5° which implies that the overall wettability across the core is the same. The contact angle values reported in Fig. 3 are the average contact measurements for the different slices. These results reflect static contact angle measurements, specifically the first contact state, which do not represent the dynamic subsurface conditions. Therefore, the contact angle values reported can vary under reservoir conditions. One additional limitation includes S_{gi}-S_{gr} data that are acquired from one experiment and consist only of one point. An alternative way to produce more S_{gi}-S_{gr} points was to use the CT scan technique that produces a fluid saturation across the sample; thus, data modelling would be more accurate, specifically, Land's coefficient calculation. Finally, the geochemical aspect, particularly the rock/CO_2/brine geochemical interactions, was neglected in this study. However, mineral dissolution is a slow process and likely does not take place in the short time of the experiments (8-9 hours). Therefore, the dissolution of the carbonate rock or precipitation of new minerals is not expected to have any notable effects on the results and CO_2 trapping during experimental work.

Future work may include additional core samples, wettability assessment at the pore scale using pore network modelling techniques, a further geochemical investigation to explore the mineralization effects and CO_2 adsorption, and finally, core-flooding experiments on core samples having different petrophysical properties.

5. Conclusions

In summary, the residual trapping mechanism was evaluated for three different limestone samples exhibiting different wettability states, e.g., water-wet, intermediate-wet, and CO_2-wet. Firstly, a delicate wettability alteration process was implemented to change the initial water-wet rock state. This process consists of treating the samples with stearic acid, an organic compound that can be found naturally in saline aquifers. Assessment of the wettability alteration was achieved through contact angle measurements and EDXS analysis. Later, a series of CO_2 core-flooding experiments were carried out at subsurface conditions ($P = 10$ MPa and $T = 323$ K) to quantify the residual CO_2 saturation for each sample. A thorough and extensive analysis was carried out to better understand the trapping mechanism influenced by rock wettability, and the key conclusions of this work are as follows:

1) Ageing limestone samples in stearic acid was found to be an effective procedure to change the wettability

to intermediate wet and CO_2-wet in 3 and 7 days, respectively. Simultaneously, the elemental composition presented an increase in the mass compositions of carbon and oxygen with a decrease in the mass composition of calcium, which further indicated the adsorption of stearate molecules on limestone surfaces.

2) The residual trapping is highly influenced by the initial wettability of the rock. The rock samples sharing the same mineralogical, petrophysical, and structural properties exhibit different CO_2 residual trapping behavior when wettability is changing. This is clearly illustrated by different S_{gi}, S_{gr}, and trapping efficiency values recorded in the core-flooding experiments for samples D1, D2, and D3.
3) Initial and residual CO_2 saturations are highly correlated with contact angles of the limestone/CO_2/brine system. After drainage, S_{gi} tends to increase with increasing the contact angle. However, after imbibition, S_{gr} is found to decrease drastically when wettability is altered towards more CO_2-wet. These two patterns are believed to occur due to the fluid configuration at the pore scale, particularly the wetting layers and the occupancy of the large areas in the pore space.
4) An inversely proportional relationship is observed between contact angle and trapping efficiency. Interestingly, trapping efficiency reaches very low values in the case of CO_2-wet, suggesting that minimal CO_2 residual trapping occurs at the core scale. Suitable conditions for the snap-off mechanism are not provided in this wettability state.
5) Although CO_2/rock interactions exist, resulting in CO_2 adsorption to the surfaces, it results in the creation of thin films surrounding the rock grains with relatively minimal capacity. These layers act as flow conduits for non-polar fluids, leading to CO_2 desaturation. Thus, changing wettability is arguably a more dominant phenomena that tends to decrease residual trapping efficiency.

In a nutshell, ignoring the wettability role in CO_2 geo-storage applications can lead to significant effects on residual gas saturation and capacity calculation. This work shed light on the degree of influence of wettability change due to organic acids on the residual trapping mechanism. Understanding this key parameter is critical and vital for storage capacity estimation, site selection, and de-risking the large-scale storage projects.

Acknowledgements

Authors at Khalifa University acknowledge the support received under award No. KU-KFUPM-2020-28. Authors at KFUPM would like to acknowledge the support received under grant No. KU-201-004 and Start-up fund Sf24002. Authors also acknowledge KU and KFUPM for facilitating this research visit.

Supplementary file

https://doi.org/10.46690/ager.2025.07.04

Conflict of interest

The authors declare no competing interest.

References

AlDhuhoori, M., Belhaj, H., AlHameli, F., et al. Assessment of mineral compositions on geo-mechanical time dependent plastic creep deformation. International Journal of Hydrogen Energy. 2024, 83: 472-490.

Ali, F., Negash, B., Ridha, S., et al. A review on the interfacial properties of caprock/CO_2/brine system-implications for structural integrity of deep saline aquifers during geological carbon storage. Earth-Science Reviews, 2023, 246: 104600.

Ali, M., Awan, F. U. R., Ali, M., et al. Effect of humic acid on CO_2-wettability in sandstone formation. Journal of Colloid Interface Science, 2021, 588: 315-325.

Ali, M., Pan, B., Yekeen, N., et al. Assessment of wettability and rock-fluid interfacial tension of caprock: Implications for hydrogen and carbon dioxide geo-storage. International Journal of Hydrogen Energy, 2022, 47(30): 14104-14120.

Al-Khdheeawi, E. A., Vialle, S., Barifcani, A., et al. Impact of reservoir wettability and heterogeneity on CO_2 -plume migration and trapping capacity. International Journal of Greenhouse Gas Control, 2017, 58: 142-158.

Al-Menhali, A. S., Krevor, S. Capillary Trapping of CO_2 in Oil Reservoirs: Observations in a Mixed-Wet Carbonate Rock. Environmental Science and Technology, 2016, 50(5): 2727-2734.

Al-Shirawi, M., Karimi, M., Al-Maamari, R. S. Impact of carbonate surface mineralogy on wettability alteration using stearic acid. Journal of Petroleum Science and Engineering, 2021, 203: 108674.

Andrew, M., Bijeljic, B., Blunt, M. J. Pore-scale contact angle measurements at reservoir conditions using X-ray microtomography. Advances in Water Resources, 2014, 68: 24-31.

Arain, Z. U. A., Aftab, A., Ali, M., et al. Influence of stearic acid and alumina nanofluid on CO_2 wettability of calcite substrates: Implications for CO_2 geological storage in carbonate reservoirs. Journal of Colloid and Interface Science, 2023, 646: 567-575.

Baban, A., Ali, M., Arif, M., et al. Effect of organic acids on CO_2 trapping in carbonate geological formations: Pore-scale observations using NMR. Energy & Fuels, 2023a, 37(4): 2983-2992.

Baban, A., Al-Yaseri, A., Keshavarz, A., et al. CO_2-brine-sandstone wettability evaluation at reservoir conditions via Nuclear Magnetic Resonance measurements. International Journal of Greenhouse Gas Control, 2021, 111: 103435.

Baban, A., Keshavarz, A., Amin, R., et al. Impact of wettability alteration on CO_2 residual trapping in oil-wet sandstone at reservoir conditions using nuclear magnetic resonance. Energy & Fuels, 2022, 36(22): 13722-13731.

Baban, A., Keshavarz, A., Amin, R., et al. Residual trapping of CO_2 and enhanced oil recovery in oil-wet sandstone core - A three-phase pore-scale analysis using NMR. Fuel. 2023b, 332(1): 126000.

Bachu, S. Drainage and imbibition CO_2/brine relative permeability curves at in situ conditions for sandstone formations in western Canada. Energy Procedia, 2013, 37: 4428-4436.

Burnside, N. M, Naylor, M. Review and implications of relative permeability of CO2/brine systems and residual trapping of CO_2. International Journal of Greenhouse Gas Control, 2014, 23: 1-11.

Chaudhary, K., Bayani Cardenas, M., Wolfe, W. W., et al. Pore-scale trapping of supercritical CO_2 and the role of grain wettability and shape. Geophysical Research Letters, 2013, 40(15): 3878-3882.

Gao, X., Yang, S., Wang, B. et al. Pore-scale modeling of multiple fluids flow transport kinetics for CO_2 enhanced gas recovery. Energy, 2025, 315: 134486.

Hu, R., Wan, J., Kim, Y., et al. Wettability impact on supercritical CO_2 capillary trapping: Pore-scale visualization and quantification. Water Resources Research, 2017, 53(8): 6377-6394.

Iglauer, S. CO_2-water-rock wettability: Variability, influencing factors, and implications for CO_2 geostorage. Accounts of Chemical Research, 2017, 50(5): 1134-1142.

Iglauer, S., Paluszny, A., Rahman, T., et al. Residual trapping of CO_2 in an oil-filled, oil-wet sandstone core: Results of three-phase pore-scale imaging. Geophysical Research Letters, 2019, 46(20): 11146-11154.

Iglauer, S., Salamah, A., Sarmadivaleh, M., et al. Contamination of silica surfaces: Impact on water-CO_2-quartz and glass contact angle measurements. International Journal of Greenhouse Gas Control, 2014, 22: 325-328.

Isah, A., Mahmoud, M., Arif, M., et al. Influence of surface cleaning on the wettability of calcite/oil/brine systems. Fuel, 2023, 351: 128908.

Juanes, R., Spiteri, E. J., Orr, F. M., et al. Impact of relative permeability hysteresis on geological CO_2 storage. Water Resources Research, 2006, 42(12): W12418.

Krevor, S., Blunt, M. J., Benson, S. M., et al. Capillary trapping for geologic carbon dioxide storage - From pore scale physics to field scale implications. International Journal of Greenhouse Gas Control, 2015, 40: 221-237.

Krevor, S., de Coninck, H., Gasda, S. E., et al. Subsurface carbon dioxide and hydrogen storage for a sustainable energy future. Nature Reviews Earth and Environment, 2023, 4(2): 102-118.

Land, C.S. Calculation of imbibition relative permeability for two- and three-phase flow from rock properties. Society of Petroleum Engineers Journal, 1968, 8(2): 149-156.

Lawal, U., Khan, H. J., Alajmei, S., et al. Evaluating CO_2 residuals in water aquifers and depleted oil reservoirs via X-ray core-flooding experiments. Energy & Fuels, 2024, 38(18): 17761-17769.

Lundegard, P. D., Kharaka, Y.K. Distribution and occurrence of organic acids in subsurface waters, in Organic Acids in Geological Processes. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 40-69, 1994.

Mirzaei-Paiaman, A., Okuno, R. Critical review on wettability, optimal wettability, and artificial wettability alteration in rock-brine-CO_2 systems for geologic carbon sequestration. Gas Science and Engineering, 2024, 132: 205499.

Mouallem, J., Arif, M., Isah, A., et al. Effect of formation brine on interfacial interaction: Implications for CO_2 storage. Fuel, 2024, 371(B): 131986.

Mouallem, J., Raza, A., Glatz, G., et al. Estimation of CO_2-brine interfacial tension using machine learning: Implications for CO_2 geo-storage. Journal of Molecular Liquids, 2023, 393: 123672.

Mouallem, J., Raza, A., Mahmoud, M., et al. Impact of petrophysical properties on CO_2 residual trapping in limestone formations. Fuel, 2025, 396: 135327.

Mutailipu, M., Liu, Y., Jiang, L., et al. Measurement and estimation of CO2–brine interfacial tension and rock wettability under CO_2 sub- and super-critical conditions. Journal of Colloid and Interface Science, 2019, 534: 605-617.

Purswani, P., Johns, R. T., Karpyn, Z. T. Impact of wettability on capillary phase trapping using pore-network modeling. Advances in Water Resources, 2024, 184: 104606.

Rahman, T., Lebedev, M., Barifcani, A., et al. Residual trapping of supercritical CO_2 in oil-wet sandstone. Journal of Colloid and Interface Science, 2016, 469: 63-68.

Rasmusson, K., Rasmusson, M., Tsang, Y., et al. Residual trapping of carbon dioxide during geological storage-Insight gained through a pore-network modeling approach. International Journal of Greenhouse Gas Control, 2018, 74: 62-78.

Rezk, G. M., Adebayo, A. R., Al-Yaseri, A., et al. Understanding gas capillary entrapment in sandstone and carbonate aquifer rocks: Impact of gas type and pore structure. Fuel, 2024, 374: 132414.

Spiteri, E. J., Juanes, R., Blunt, M. J., et al. A new model of trapping and relative permeability hysteresis for all wettability characteristics. SPE Journal, 2008, 13(3): 277-288.

Spurin, C., Callas, C., Darraj, N., et al. The importance and challenges associated with multi-scale heterogeneity for geological storage. InterPore Journal, 2025, 2(1): IPJ260225-2.

Stevar, M., Bohm, C., Notarki, K., et al. Wettability of calcite under carbon storage conditions. International Journal of Greenhouse Gas Control, 2019, 84: 180-189.

Teng, Y., Wang, P., Xie, H., et al. Capillary trapping characteristics of CO_2 sequestration in fractured carbonate rock and sandstone using MRI. Journal of Natural Gas Science and Engineering, 2022, 108: 104809.

Wang, Y., Wang, J., Liu, H., et al. Effects of acid–rock reaction on physical properties during CO_2-rich industrial waste gas (CO2-rich IWG) injection in shale reservoirs. Petroleum Science, 2024, 21(1): 272-285.

Wei, B., Wang, B., Li, X., et al. CO_2 storage in depleted oil and gas reservoirs: A review. Advances in Geo-Energy Research, 2023, 9(2): 76-93.