

Original article

The influence of methyl orange on the CO₂-brine wettability of organic-acid-aged calcite samples: Implications for CO₂ geo-storage

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Abstract:

The underground storage of CO₂ in a depleted carbonate formation is a suitable method for limiting its anthropogenic release and minimize global warming. The rock wettability is an essential factor controlling the mechanisms of CO₂ trapping and its containment safety in the geo-storage formation. The geo-storage rock contains innate organic acids which alters the wettability of the rock surface from the hydrophilic condition to the hydrophobic state, thus reduce the CO₂ storage capacity. In this study, methyl orange which is a toxic dye that is generally released into environment was used as wettability modifier to change the wettability of stearic acid aged calcite (oil wet) to water wet. This study uses the contact angle technique (sessile drop method) to examine the effects of various concentration of methyl orange (10-100 mg/L) on the wettability of the CO₂/brine/stearic-acid aged calcite system under geo-storage conditions (i.e., temperatures of 25 and 50 °C and pressures of 5-20 MPa). The results indicate that the advancing and receding contact angles (θ_a and θ_r) of the organic-acid contaminated rock surface were drastically reduced upon exposure to methyl orange, attaining the minimum values of 62° and 58° respectively, in the presence of 100 mg/L methyl orange at 20 MPa and 50 °C. Thus, the present results suggest that rather than discharging methyl orange into the environment, it could be injected into underground reservoirs in order to reduce the level of environmental pollution and at the same time increase the CO₂ storage capacity of carbonate formations.

1. Introduction

The global population growth and industrial revolution are two main contributing factors to the significant increase in carbon dioxide (CO₂) emissions and climate change (Anwar et al., 2019; Nunes, 2023). Hence, the geo-storage of CO₂ in geological formations has been identified as a crucial strategy for mitigating the anthropogenic emissions of CO₂ into the atmosphere and attaining the target of net zero carbon emissions and CO₂ free global economy (Ajayi et al., 2019; Ali et al., 2022a; Rasool et al., 2023). Different types of CO₂

geo-storage media have been identified, including depleted hydrocarbon reservoirs, salt caverns, unmineable coal seams, and saline aquifers (Keshavarz et al., 2018; Memon et al., 2022; Baban et al., 2023). Among these storage sites, depleted oil and gas fields and sedimentary saline aquifers stand out due to their wide geographical distribution, reasonably high permeability and porosity, high storage capacity, and relatively low permeable shales or suitable cap rocks. However, the wettability of sedimentary rocks such as carbonates or sandstones has significant implication for the efficiency and security of the

CO₂ storage process in these formations (Iglauer et al., 2015; Arif et al., 2017; Stevar et al., 2019; Le et al., 2020; Abdi et al., 2022).

In general, there are four types of CO₂ trapping mechanisms in the host rock that could immobilize CO₂ in the storage formation, these includes: Residual, structural, solubility, and mineral trapping, (Zhang and Song, 2014; Kelemen et al., 2019; Al Hameli et al., 2022). Among these mechanisms, structural trapping and residual/capillary trapping are the major trapping mechanisms contributing to long-term immobilization. At the commencement of CO₂ injection, the injected CO₂ pushes the resident formation brine away to occupy the pore spaces. However, as the injection pressure is relaxed, the buoyant supercritical CO₂ migrates to the surface due to its lower viscosity and density relative to the resident brine. Once the CO₂ injection stops, re-imbibition of brine into the pore space occurs, thereby resulting in the co-existence of two phases in the pores. This process generates capillary forces that are capable of trapping and immobilizing a portion of the injected CO₂, which prevents or slows down the upward migration of the free (fluid) CO₂ phase. This phenomenon is known as the residual trapping of CO₂. Also, the presence of low permeable geological overlying layers (seals) can prevent the vertical or lateral expansion of the stored CO₂, thereby providing structural trapping. Generally, the effects of CO₂ trapping mechanisms depend on the hydrophilicity of the host rock.

The results of some previous research on the wettability of brine/rock/CO₂ systems are summarized in Table 1. These studies have shown that increased water wettability is favorable for the residual and structural trapping of CO₂ (Espinoza and Santamarina, 2010; Mills et al., 2011; Farokhpoor et al., 2013a; Arif et al., 2017; Stevar et al., 2019). Temperature and pressure have significant effect on residual/structural trapping but the impacts of pressure on contact angle values and host-rock wettability was most significant. Contact angle generally increased with increasing pressure suggesting that host rock could become more hydrophobic with increasing storage depth. Overall, while some clean carbonate analog minerals, particularly calcite, can be water wet under ambient conditions, most carbonate formations are hydrophobic due to the inherent presence of organic acids. The binding energy of these organic molecules on the calcite surface is larger than that of brine molecules. Moreover, the presence of long-chain hydrocarbons with carboxyl (-COOH) end groups will decrease the CO₂ containment safety of the oil-wet calcite.

Previous studies have also shown that the surface of calcite becomes more hydrophobic with the existence of organic acids such as those inherent in geo-storage formations, thereby decreasing the CO₂ storage capacity of the carbonate formation under realistic subsurface conditions. For example, Al-Yaseri et al. (2022) showed that the contact angle increased from 97.9° to 136.5° when the calcite surface was aged in 10⁻² mol/L stearic acid, while Arain et al. (2023) found that the modification of the calcite surface with stearic acid changes the wettability to the CO₂-wet condition. Moreover, Ivanova et al. (2022) conducted micro-scale contact angle measurements of the surface of calcite after aging with palmitic, stearic, and

naphthenic acids, and found that the wettability of the organic-acid aged calcite surface shifted to the more hydrophobic condition.

Over 50% of the depleted reservoirs with CO₂ storage potential are classified as carbonate rocks, which can be either intermediate or oil wet. Therefore, it is important to devise a means of decreasing the hydrophobic conditions of such reservoirs in order to increase the CO₂ geo-storage capacity. Some studies have shown that the wettability of CO₂ storage reservoirs that are exposed with different organic acids can be altered to the hydrophilic state by injecting various chemicals into the formation, thereby increasing its CO₂ storage capacity. For instance, Kanj et al. (2020) used dynamic and static contact angle measurements to demonstrate that an oil-contaminated carbonate rock became water-wet when exposed to a carbon nanofluid solution. Meanwhile, Roustaei and Bagherzadeh (2015) found that the contact angle of carbonate rock dropped upon treatment with increasing concentrations of SiO₂ nanoparticles (1-6 g/L).

Further, the present authors recently demonstrated that the surface of organic-acid contaminated rock can be altered into the hydrophilic (water-wet) state by treatment with various concentrations of methylene blue and methyl orange (MO) (10-100 mg/L each) (Alhammad et al., 2022, 2023a, 2024). However, those studies were conducted using a quartz substrate and the measurement of contact angle was conducted in the absence of CO₂ for enhanced oil recovery purposes. Meanwhile, the effect of MO on the wettability of the CO₂/calcite/brine system for enhanced CO₂ containment security of the carbonate formation is yet to be explored. Notably, MO is a wastewater chemical that must be treated properly before disposing it into the environment. Therefore, its usage as a wettability modifier for carbonate formations could reduce the environmental pollution that is associated with discharging a large volume of MO into the wastewater while simultaneously enhancing the structural and residual trapping capacities of the geo-storage formations.

2. Methods and materials

2.1 Materials

The calcite (Iceland spar) used as a carbonate mineral representative rock was supplied by Ward's Science (Rochester). Sodium chloride (NaCl; purity ≥ 99 mol fraction) was bought from Sigma-Aldrich (Australia) and was used to prepare various brine solutions (0, 0.1, 0.2, and 0.3 M). Nitrogen gas and carbon dioxide (purity = 99.9 mol% each) were supplied by BOC (Australia). The nitrogen was used to dry the calcite substrates after cleaning them with deionized water (DI), while the CO₂ was used at supercritical condition for the contact angle measurements.

A constant stearic acid concentration (10⁻² mol/L) was prepared by using n-decane as the base solution. The stearic acid and decane were more than 98% pure and were supplied by Sigma Aldrich. The MO (with 85 wt.% dye content) was obtained from Sigma-Aldrich, and its chemical structure is shown in Fig. 1. This was utilized to modify the surface wettability of the stearic-acid-aged calcite.

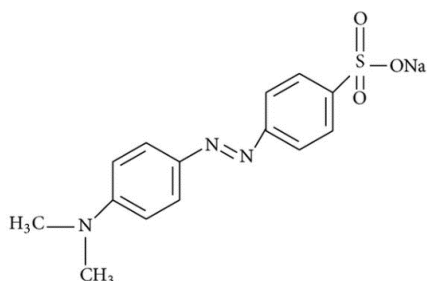
Table 1. Results of some previous research on the wettability of brine/rock/CO₂ systems.

Rock (Reference)	Technique	Pressure (MPa)	Temperature (°C)	Salinity	Findings
Weyburn limestone (Yang and Gu, 2008)	Sessile drop	0.1-33.6	27 & 58	Brine (6.6 wt.%)	The contact angle (CA) dropped with temperature and raised with pressure; CO ₂ dissolution resulted in an increasing CA with temperature
Calcite & quartz (Espinoza and Santamarina, 2010)	Sessile drop	0.1-6.43	147.7	NaCl (20 wt.%) & DI	The CA of hydrophobic quartz increased from 85° to 90° with the increase in pressure from 0.1 MPa to 6.43 MPa at a constant temperature; In the presence of NaCl, the CA increased by almost 4° for calcite and 20° for quartz.
Dolomite, sandstone, calcite & limestone (Jaeger et al., 2010)	Sessile drop	19.3, 20.7, & 21.2	161.8	Seawater (synthetic; 33,988 ppm)	The CA increased with pressure. In the case of calcite, CA values increased from 80° to 109° and, as the pressure was increased from 0 to 19.3 MPa.
Calcite, mica & quartz (Mills et al., 2011)	Captive bubble	6 & 13	40	Brine (35,000 ppm)	The CA of mica and calcite decreased with pressure, whereas that of quartz increased with pressure
Calcite, quartz, mica & rousse caprock (Broseta et al., 2012)	Captive bubble	0.5 & 14	Up to 140	NaCl (4, 40 & 350 g/L)	The CA increased with pressure for calcite, quartz, and Rouse caprock; The wettability ranged from strongly hydrophilic to intermediate hydrophilic condition.
Calcite, mica & quartz (Seyyedi et al., 2015)	Captive bubble	0.7-24.1	37.8	Sea-brine (54,597 ppm)	The advancing CA of calcite reduced from 144° to 97° as pressure was increased from 0.7-24.1MPa.
Calcite ^a (Al-Anssari et al., 2017a)	Tilted plate goniometric	0.1-20	146.7-172.8	/	The CA of hydrophobic calcite was reduced from 147° to 41° when treated with nanofluids; With increasing pressure and salinity, CA increased, but with increasing temperature, CA decreased.
Calcite ^b (Al-Anssari et al., 2017b)	Tilted plate	0-20	23-70	NaCl (20 wt.%)	The calcite surface altered from intermediate water-wet to strongly hydrophilic condition when treated with nanofluid
Limestone, berea sandstone & quartz (Mutailipu et al., 2019)	Sessile drop	3-15	147.8-189.4	NaCl (1.98 mol/kg) & DI	The CA raised by around 5°-13° as the state of CO ₂ changed from subcritical to supercritical.
Calcite (Stevar et al., 2019)	Sessile drop	0-30	147.8-189.4	NaHCO ₃ (molality = 1 mol·kg ⁻¹)	The calcite surface is mostly wetted by brine but can become intermediate or weakly CO ₂ wet at a pressure of almost 10 MPa and a low temperature of 148.9 °C.
Calcite (Chen et al., 2019)	Interfacial tensiometer (Vinci IFT 700)	20.7-24.1	25	1.0 mol/L CaCl ₂	The CA decreased in the presence of carbonated and acidic brines.
Calcite (Le et al., 2020)	Molecular dynamic simulation	20	50	0.1-3 M NaCl	The attraction between the calcite surface and a supercritical CO ₂ droplet increased with increasing concentration of NaCl.
Calcite ^c (Aftab et al., 2023)	Sessile drop	0.1, 10, & 25	161.7	NaCl (10 wt.%)	The stearic-acid aged calcite became hydrophilic at an optimum Al ₂ O ₃ nanofluid concentration of 0.25 wt.%.
Indiana limestone ^d (Sakthivel et al., 2024)	Interfacial tensiometer (IFT-700)	0.1-20.7	20-80	Formulated seawater (1.2 M)	In the presence of 1,000 ppm carbon nanodots solution, the CA of hydrophobic carbonate was dropped from 122° to 86°.

Notes: *a* denotes treated with SiO₂ nanoparticles modified with sodium Dodecylsulfate, *b* denotes treated with SiO₂ nanoparticles, *c* denotes treated with stearic acid and Al₂O₃ nanofluids, *d* denotes treated with carbon nanodots.

Table 2. The rock-eval pyrolysis values of the pure calcite and the calcite aged with stearic acid before and after exposure with MO.

Sample	Quantity of sample (mg)	S1 (mg/g rock)	S2 (mg/g rock)	T_{max} (°C)	TOC (%)
Pure calcite	60	0.16	0.25	320	0.1
Calcite aged in 100 mg/L stearic acid	60	2.08	2.61	407	0.44
Calcite aged in 100 mg/L stearic acid and modified with 100 mg/L MO	60	0.53	0.45	320	0.2

**Fig. 1.** The chemical structure of MO (Lai et al., 2015).

2.2 Cleaning and aging procedure

To remove all surface contaminants before conducting the experiments, the calcite substrates were cleaned with DI water, dried in an oven at 60 °C for one hour, and then exposed to air plasma for 15 min (Al-Ansari et al., 2017c; Alnili et al., 2018; Al-Yaseri et al., 2022). After that, the substrates were soaked in 2 wt.% NaCl solution, and HCl was added dropwise to obtain a pH of 4. To enhance the surface adsorption of stearic acid and simulate realistic reservoir conditions, the calcite substrates were kept in this solution for 30 min. Subsequently, the ionized calcite substrates were exposed to nitrogen to remove any remaining water from the calcite surface. Afterwards, the ionised calcite samples were submerged in 200 mL of n-decane/stearic acid (10^{-2} mol/L) solution and left in the oven at 60 °C for 1 week to stimulate the geological conditions of the reservoir, where the naturally-occurring organic acids make the surface of calcite oil wet (Bikkina, 2011; Farokhpoor et al., 2013b; Arain et al., 2023). Finally, the calcite aged with stearic acid substrates were immersed in different MO concentrations (10-100 mg/L) and placed in the oven for 1 week in order to change the wettability of the stearic-acid contaminated calcite to its original water-wet condition (Alhammad et al., 2023a, 2023b).

2.3 Contact angle measurements

CO₂/brine contact angles on the stearic-acid-aged calcite samples before and after MO-modification were measured under various reservoir conditions (i.e., $T = 25$ and 50 °C, $P = 5$ -20 MPa, and salinity = 0-0.3 M) by using the sessile drop tilted plate setup shown schematically in Fig. 2. For this

process, the optical cell was first cleaned with DI water and then various brine concentrations (0, 0.1, 0.2, and 0.3 M) were injected via a high-pressure high-temperature pump. The plate was tilted at angle of 17° to obtain a suitable drop of brine on the aged calcite surface. The substrate was placed on top of the tilted plate and the cell was closed. Then, the cell was gradually raised to the desired temperature (25 or 50 °C). After this, the pressure of CO₂ was set to 5, 10, 15, or 20 MPa, and a droplet of degassed brine was laid on the aged calcite surface at the desired temperature and pressure.

Subsequently, the contact angle image was recorded using a video camera. Then, before the drop of brine slide down, the software of ImageJ was utilized to measure the receding and advancing contact angles at the trailing and leading edge respectively. This experimental method was designed by the previous researchers (Wani et al., 2018; Ali et al., 2019; Naghizadeh et al., 2020; Alnough et al., 2021; Hosseini et al., 2022; Alhammad et al., 2023a).

3. Results and discussion

3.1 The total organic content and other pyrolysis parameters of the various samples

A version 6 rock-eval pyrolysis turbo device was used to measure the total organic content (TOC) and other pyrolysis parameters of the pure calcite, and the calcite aged with stearic acid before and after exposure with MO at 100 mg/L. For this procedure, the pure calcite substrate and the MO/stearic-acid-aged substrates were each crushed and ground to 80 mesh size. Then, 60 ± 3 mg of each powdered sample was pyrolyzed at 200-650 °C in an atmosphere of N₂ at a heating rate of 30 °C/min.

As shown in Table 2 and Fig. 3, 0.1% of organic matter remained in the pure calcite after pyrolysis, whereas the MO/stearic-acid-aged samples exhibited TOC values of 0.2%-0.44%. In the rock-eval pyrolysis analysis (Fig. 3), the quantity of hydrocarbon (in mg/g of rock) already present is indicated by the peak labeled S1, while the peak S2 indicates the amount of additional hydrocarbons produced due to thermal pyrolysis. The T_{max} value in Table 2 corresponds to a crude measurement of thermal maturity (Ali et al., 2021). Notably, S1 and S2 were increased in the stearic-acid aged samples compared to the pure calcite (Fig. 3).

In detail, the TOC value increases from 0.1% for pure cal-

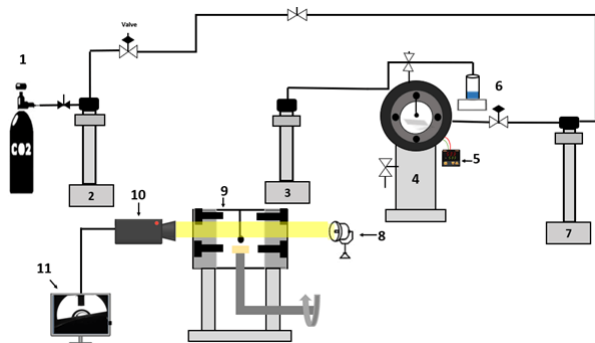


Fig. 2. A setup of contact angle measurement: (1) Source of CO₂; (2) syringe pump of CO₂; (3) syringe pump of brine; (4) front view of HPHT cell; (5) controller of temperature connected to electrical heater; (6) drainage/refill system; (7) wet CO₂ syringe pump; (8) light source, (9) side view of HPHT cell, (10) video camera; (11) software of ImageJ to analyze the contact angles (Alhammad et al., 2023a).

cite to 0.44% for the stearic-acid-aged calcite due to the presence of the stearic acid on the surface of calcite. However, the TOC value is reduced from 0.44% for the stearic-acid-aged calcite to 0.2% upon modification with MO, thereby suggesting that the surface wettability has been reversed to the initial hydrophilic state of the pure calcite. Moreover, the higher TOC values obtained from the rock eval pyrolysis analysis demonstrate an increase in CO₂ wetting for the stearic-acid aged calcite (Pan et al., 2020), thereby confirming that the carbonate rock became more oil-wet (hydrophobic) in the presence of organic acid.

However, the lower TOC content of the MO-modified substrate suggests that the calcite surface tends to become more water-wet (hydrophilic) after this treatment. The amount of pyrolyzed carbon is computed from the amounts of hydrocarbon compounds released in peak S1 (which is observed at temperatures of up to 300 °C) and S2 (300-650 °C), assuming that they contain about 83% of the organic carbon (Ordoñez et al., 2019). Thus, the results in Fig. 3 indicate that more hydrocarbons (4,690 ppm) were released from the stearic-acid-aged sample than from the MO-modified sample (980 ppm) and from the pure calcite (410 ppm).

3.2 The surface morphologies and elemental compositions of the various samples

The composition and topography of the rock surface before and after stearic-acid aging and MO modification were examined via scanning electron microscopy (SEM; instrument model, manufacturer). In addition, the chemical (elemental) compositions of the various samples were elucidated by energy dispersive X-ray spectroscopy (EDS; instrument model, manufacturer).

The images of SEM of the pure calcite, the calcite aged with stearic acid, and the MO-modified calcite are presented in Fig. 4, while the corresponding EDS results are presented in Fig. 5. Here, the pure calcite exhibits a smooth surface (Fig. 4(a)) and is composed of calcium, oxygen, and carbon (Fig. 5(a)). However, after aging with stearic acid, a rough surface

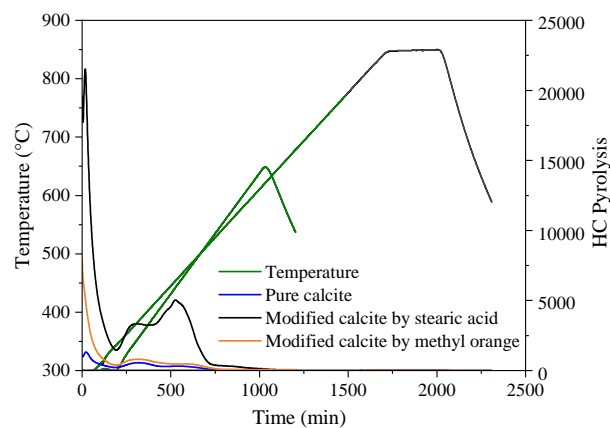


Fig. 3. The rock-eval pyrolysis analysis of the pure calcite and the calcite aged with stearic acid before and after exposure with MO.

is observed due to the presence of large organic molecules deposits (Fig. 4(b)), while the amount of carbon is significantly increased due to adsorption of stearic acid, the amounts of calcium and oxygen decreased (Fig. 5(b)), thus the wettability of the stearic acid aged calcite become hydrophobic. These results are consistent with those of previous studies (Ali et al., 2019; Al-Shirawi et al., 2021). Notably, the quantity of large organic acid deposits is somewhat reduced after MO modification (Fig. 4(c)), and presence of different elements such as carbon, oxygen, sulphur, sodium, nitrogen, and calcium are observed in the EDS result (Fig. 5(c)). This is due to the adsorption of MO on the calcite surface. This confirmed the presence of MO on the surface of stearic-acid aged calcite which therefore changed the wettability of stearic acid aged calcite to hydrophilic condition. This is consistent with previous study by the present authors (Alhammad et al., 2023a), suggesting that MO is a favorable wettability modifier for organic molecules contaminated rocks.

3.3 The surface functional groups of the various samples

The functional groups present in the various substrates were elucidated by Fourier transform infrared (FTIR) spectroscopy (instrument model, manufacturer) under $\lambda =$ irradiation in the full scan range of 400-4,000 cm^{-1} (So et al., 2020; Santos et al., 2021; Calandra et al., 2022).

The FTIR spectra of the pure calcite, the stearic-acid-aged calcite and the MO-modified stearic-acid-aged calcite samples are presented in Fig. 6. Here, the pure calcite (blue profile) exhibits multiple adsorptions between 500 and 1,400 cm^{-1} corresponding to the carbonate asymmetric stretching vibrations and out-of-plane bending vibrations. This result is similar to results of previous studies by Hajji et al. (2017) and Chakrabarty and Mahapatra (1999), who reported that pure calcite exhibits adsorptions at 718-1,425 and 713-874 cm^{-1} .

After aging with stearic acid, however, a new adsorption was observed between 2,850 and 2,954 cm^{-1} (red profile, Fig. 6). This adsorption corresponds to the vibration of stretching of the $-\text{CH}_3$ group, that is responsible for changing the wettability to the hydrophobic condition. This is consistent

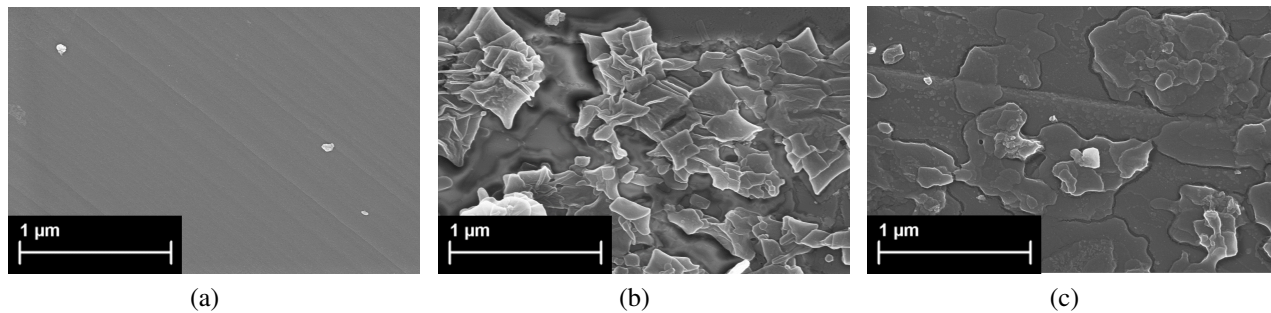


Fig. 4. The SEM images of (a) the pure calcite, (b) the calcite aged with stearic acid, and (c) calcite modified with MO.

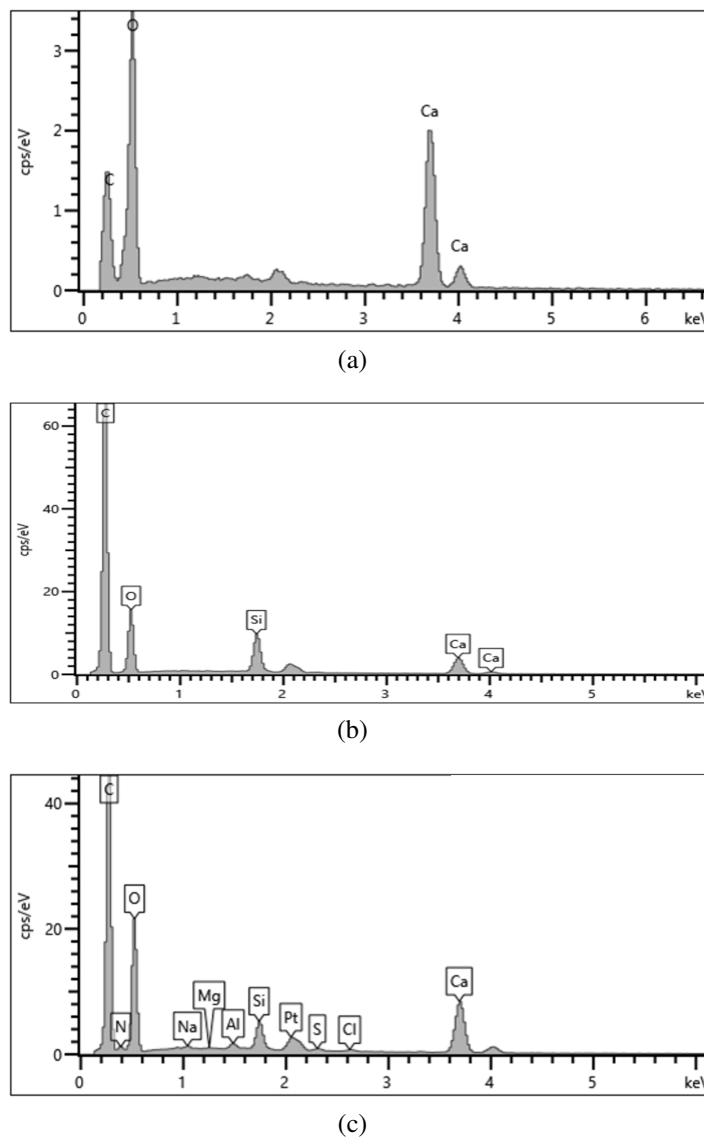


Fig. 5. The EDS results for (a) the pure calcite, (b) the calcite aged with stearic acid, and (c) calcite modified with MO.

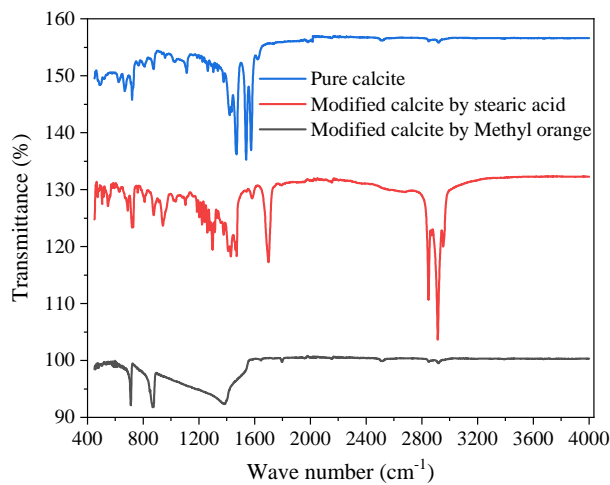


Fig. 6. The FTIR spectra of the pure calcite, the calcite aged with stearic acid, and the MO-modified calcite.

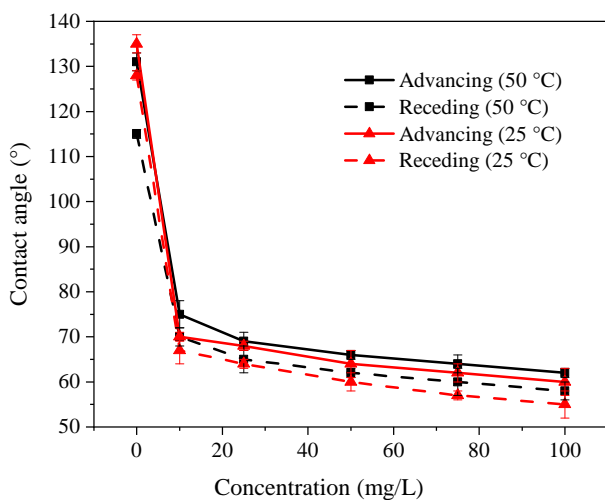


Fig. 7. Different MO concentrations on the θ_a and θ_r values of the calcite aged with stearic acid at a constant pressure and salinity 20 MPa and 0.3 M NaCl.

with the results of Hajji et al. (2017), who observed an adsorption band between 2,872 and 2,924 cm^{-1} due to the presence of C–H bonds on the calcite surface after stearic acid aging. However, when the stearic-acid-aged calcite is modified with MO, the asymmetric stretching vibration of CH_3 is reduced (black profile, Fig. 6). This is consistent with previous study by the present authors, which showed that $-\text{CH}_3$ was entirely absent when organic-acid contaminated quartz was aged in MO. These FTIR results further demonstrate that the wettability of calcite is changed to the hydrophilic condition in the presence of MO.

3.4 The effect of MO concentration on CO_2 /calcite/brine wettability

The effects of different concentrations of MO (10-100 mg/L) on the advancing and receding contact angles (θ_a and θ_r) of the calcite aged with stearic acid at 20 MPa and 0.3 M NaCl at temperatures of 25 and 50 °C are shown in Fig. 7.

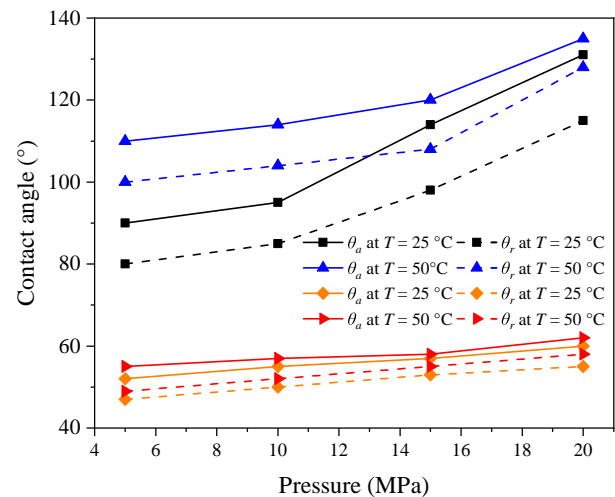


Fig. 8. Different pressure and temperature on the θ_a and θ_r values of calcite aged with stearic acid at a concentration of brine of 0.3 M before (black and blue symbols) and after (orange and red symbols) exposed with 100 mg/L MO.

Here, when the MO concentration is 0 mg/L, with the increase in temperature, both the θ_a and θ_r values are seen to increase due to the presence of the carboxylic molecule on the calcite surface, which renders it oil wet. In detail, the θ_a value is increased from 131° to 135°, while the θ_r value increased from 115° to 135° with the increase in temperature from 25 to 50 °C.

However, after exposure to various concentrations of MO, the calcite surface became water wet. For example, at $T = 25$ °C, the θ_a value reduced from 70° with 10 mg/L MO to 60° with 100 mg/L, while the corresponding θ_r values decreased from 67° and 55°, respectively. Similarly, at $T = 50$ °C, the θ_a value reduced from 75° to 62°, and the θ_r value decreased from 70° to 58°, across the same range of MO concentrations. These results indicate that the calcite surface becomes more hydrophilic as the concentration of MO is increased, with the optimum concentration being 100 mg/L.

These results are consistent with those obtained in our previous study using a quartz substrate, where significant reductions in both contact angles were observed after aging in various concentrations of MO. This reduction in contact angle is due to the presence of two hydrophilic groups ($-\text{N}=\text{N}-$ and $-\text{SO}_3-$) on both the calcite and quartz surfaces after aging with MO (Isac-García et al., 2015; Alhammad et al., 2022, 2023a). Thus, the injection of MO into the underground reservoir could contribute to increasing the CO_2 storage capacity and reducing the CO_2 emissions into the atmosphere.

3.5 The effect of temperature and pressure on CO_2 /stearic acid aged calcite/brine wettability before and after MO modification

The effects of various pressures (5-20 MPa) and temperatures (25 and 50 °C) on the θ_a and θ_r values of the calcite aged with stearic acid before and after exposure to MO are presented in Fig. 8. Thus, at a constant temperature of 25 °C, the θ_a value of the unmodified stearic-acid-aged calcite

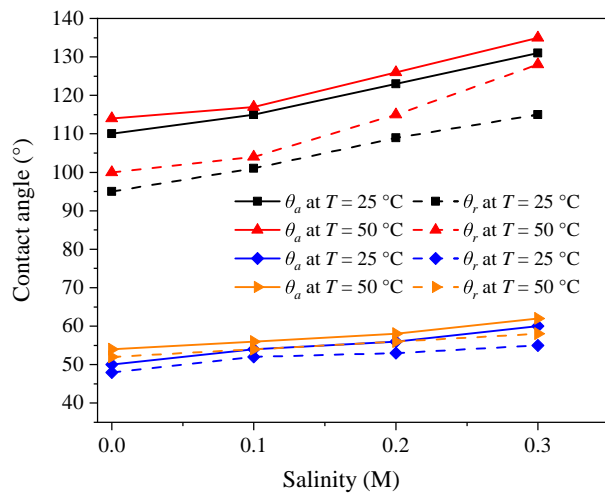


Fig. 9. The effects of various salinities on the θ_a and θ_r values of the calcite aged with stearic acid samples at 25 and 50 °C and 20 MPa before (black and red symbols) and after exposure with 100 mg/L MO (blue and orange symbols).

(solid black line) increased from 90° to 131° as the pressure was increased from 5 to 20 MPa, while the θ_r value (dashed black line) increased from 80° to 115°. Similarly, at the higher temperature of 50 °C, the θ_a value (solid blue line) increases from 110° to 135°, and the θ_r value (dashed blue line) increases from 100° to 128°, across the same pressure range. These results indicate that the calcite is highly disposed to become CO₂ wet in the presence of the organic acid. In particular, at high-temperature and high-pressure conditions of the typical geo-storage formation, where organic acids are inherently present, the high θ_r value suggests that capillary leakage may occur, while the high θ_a value suggests that the residual trapping of CO₂ could become unfavorable. These results are consistent with those of previous studies (Madsen and Lind, 1998; Iglauer et al., 2015; Ali et al., 2022b), and are generally attributed to the covalent interactions between the groups of hydroxyl of the calcite substrate and the stearic acid molecules (Al-Busaidi et al., 2019).

However, after modification with MO, the θ_a and θ_r values are seen to decrease significantly relative to those of the unmodified, stearic-acid-aged calcite. We also observed slight increase in contact angles with the increase in pressure and temperature. Thus, when the pressure is increased from 5 to 20 MPa at a constant temperature of 25 °C, the θ_a value (solid orange line) increases from 52° to 60°, while the θ_r value (dashed orange line) increases from 47° to 55°. These correspond to increases of only 8° compared to around 35 to 41° for the unmodified, stearic-acid aged calcite. Similarly, at $T = 50$ °C, the θ_a and θ_r values of the MO-modified sample increase from 55° to 62°, and from 49° to 58°, respectively, under the same increase in pressure. These observations are also consistent with previous studies (Alhammad et al., 2023a). For example, the present authors previously found that the θ_a value of MO-modified, stearic-acid aged quartz was increased from 49° to 65°, and the θ_r increased from 45° to 58°, as the pressure was increased from 10 to 20 MPa. Similarly, Arain et al. (Arain et al., 2023) found that when stearic acid

aged calcite was modified with a maximum concentration of alumina nanofluid (0.25 wt.%), the θ_a and θ_r values were increased from 27.4° to 68.9°, and from 25.7° to 60.3°, respectively, as the pressure was increased from 10 to 20 MPa at a temperature of 323 K.

3.6 The effect of brine salinity on CO₂/stearic acid aged calcite/brine wettability before and after MO modification

The effects of various brine salinities on the θ_a and θ_r values of the stearic-acid-aged calcite before and after exposure to MO are shown in Fig. 9. Thus, at a constant temperature of 25 °C, the θ_a value of the unmodified, stearic-acid-aged calcite (solid black line) increases from 110° to 131° as the salinity is increased from 0 to 0.3 M, while the θ_r value (dashed black line) increases from 95° to 115° across the same salinity range. Similarly, at $T = 50$ °C, the θ_a value (solid red line) increases from 114° to 135°, while the θ_r value (dashed red line) rises from 100° to 128° with the increase in salinity. These results suggest that the stearic-acid-aged calcite surface becomes more hydrophobic at higher salinity.

A similar trend is observed after MO modification, although the actual contact angle values at each salinity are much lower than those observed before the modification. Moreover, the amount of change in the contact angle according to salinity is much less after MO modification, so that the calcite surface remains intermediate wet. For instance, at a constant temperature of 50 °C, the θ_a value (solid orange line) increases from 54° to 62°, and the θ_r value (dashed orange line) raised from 52° to 58°, as the brine salinity is raised from 0 to 0.3 M. This observation is similar with previous work on the quartz/CO₂/brine system, where the θ_a and θ_r values of the MO-modified quartz increased from 37° to 50°, and from 32° to 46°, respectively, as the concentration of NaCl was raised from 0 to 0.3 M. Similarly, Arif et al. (2017) noticed that the θ_a of calcite increased from 86° to 95° as the salinity was increased from 5 to 20 wt.% NaCl. In addition, Al-Anssari et al. (2016) observed an increase contact angle of the calcite/brine/air system with increasing salinity from 0 to 20 wt.% NaCl. This is attributed to ion adsorption on the calcite substrate, which can create an electrical double layer and change the intermolecular forces between the solid and liquid (Silvestri et al., 2019).

4. Conclusions

The calcite-brine-CO₂ wettability system plays a significant role in determining the storage capacity and CO₂ containment security of carbonate formations. Organic acids are generally found in real reservoir conditions and can change the surface wettability of the carbonate formation from hydrophilic condition to hydrophobic condition. Therefore, the injection of an additional chemical is required to increase the capacity storage of CO₂. Hence, the present study was conducted to provide insights into the effects of MO in altering the wettability of calcite after aging with stearic acid. To this end, the advancing and receding contact angles of the stearic-acid-aged calcite were measured at various temperatures (25

and 50 °C), pressures (5-20 MPa), and salinities (0-0.3 M) before and after exposure with MO. The results indicated that when calcite is aged with stearic acid under ambient conditions, the advancing and receding contact angles are 131° and 115°, respectively, whereas the subsequent modification with the optimum amount of MO (100 mg/L) resulted in decreased advancing and receding contact angles to 60° and 58°, respectively, under the same conditions. The increasing hydrophilicity of stearic-acid aged calcite in presence of MO can be attributed to the solubility of MO in stearic acid which resulted in increasing surface roughness of calcite surface. This phenomenon is favorable for the retention of water molecules the rock surface to promote the restoration of rock wettability to original hydrophilic state. This study demonstrates that the injection of MO into underground reservoirs, rather than releasing it into the environment, can provide a significant solution for reducing the emissions of greenhouse gases and achieving large-scale CO₂ storage and decarbonized economy.

5. Recommendation and future work

This research we have used a pure calcite which is a representative of carbonate rock and stearic acid to mimic presence of organic molecules on surface of geo-storage rocks. However, these selections are not fully representative of the heterogeneity of the geo-storage rock as the real reservoir rock is heterogenous at geo storage conditions, and the geological formation contains different organic acids and different kind of rock minerals. Thus, effect of reservoir rock heterogeneity and different organic acids present in geo storage formations should be evaluated in future studies to avoid over prediction of wettability modification properties of MO.

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Conflict of interest

The authors declare no competing interest.

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