Asian Journal of Science, Engineering and Technology (AJSET)
eISSN: 3006-6980 (online)
https://ideapublishers.org/index.php/ajset
Vol. 4, No. 1 (January-December), 2025, pp. 153-172
https://doi.org/10.47264/idea.ajset/4.1.10
Original Research Article

Optimising wettability alteration in carbonate reservoirs using hybrid low-saline brine formulations for enhanced oil recovery

Faisal Hussain Memon*[1] | Ghulam Abbas[1] | Muhammad Furqan Qureshi[2] | Abdul Samad Shaikh[1] | Tahir Ali Soomro[3] | Abdul Haque Tunio[2]

1. Department of Petroleum and Natural Gas Engineering, Mehran University of Engineering and Technology, S. Z. A. B. Campus, Khairpur Mirs, Sindh, Pakistan.
2. Institute of Petroleum and Natural Gas Engineering, Mehran University of Engineering and Technology, Jamshoro, Sindh, Pakistan.
3. Petroleum Division, Directorate General of Petroleum Concession (DGPC), Islamabad, Pakistan.

*Corresponding Author Email: faisalhussain@muetkhp.edu.pk

Article History

Received:
07-Jan-2025

Revised:
27-Apr-2025

Re-revised:
14-May-2025

Accepted:
19-May-2025

Published:
10-Nov-2025

Updated:
11-Dec-2025

Abstract: The study investigates the impact of hybrid low-saline brine (LSB) formulations on wettability alteration to enhance oil displacement efficiency in carbonate reservoirs, which are challenging due to their oil-wet nature. Five distinct hybrid LSBs injection schemes with varying salt concentrations, xanthan polymer, silica nanoparticles, and reef salts were developed to modify the carbonate core wettability. Fourier Transform Infrared spectroscopy (FTIR) was utilised to validate the structural and mineralogical alterations of the designed schemes. Whereas contact angle (CA) measurements determined the shifts in wettability. The results exposed that surface treatment (ageing) has modified the rock surface chemistry of the core samples, shifting wettability from oil-wet to water-wet states through rock-brine-oil interactions. Higher temperatures and salinity concentrations facilitated more pronounced wettability changes, with CA values decreasing from 126° to 80°. Notably, scheme 5 with xanthan polymer, reef salts, and silica nanoparticles showed the greater wettability adjustment, decreasing CA by more than 30° at 60°C. The findings highlight the significance of hybrid LSB formulations for temperature and interfacial tension sensitivity to control wettability under complex reservoir conditions. This study verifies the effectiveness of the designed hybrid LSB formulations in shifting wettability, providing a pathway to enhance oil recovery (EOR) techniques in carbonate reservoirs.

Keywords: Wettability alteration, Hybrid low saline brine formulation, Contact angle measurement, Enhanced oil recovery, Carbonate reservoir.

How to Cite: Memon, F. H., Abbas, G., Qureshi, M. F., Shaikh, A. S., Soomro, T. A., & Tunio, A. U. (2025). Optimising wettability alteration in carbonate reservoirs using hybrid low-saline brine formulations for enhanced oil recovery. *Asian Journal of Science, Engineering and Technology (AJSET), 4*(1), 153-172. https://doi.org/10.47264/idea.ajset/4.1.10

1. Introduction

Energy is the most substantial parameter for sustainable development, specifically in developing countries, where demand is increasing rapidly due to continuous urbanisation. Fossil fuels like natural gas, oil, and coal are the main sources of energy, while hydrocarbons remain inevitable for both developed and developing countries, despite diversification of energies (Kartal, 2022; Majeed & Mahesar, 2016). Present energy demands exceed available reserves, causing challenges for a continuous energy supply. Renewable energy sources are inadequate to bridge the gap between demand and supply. Effective utilisation of hydrocarbon-based fossil fuels is a viable and sustainable solution to address this severe energy crisis (Asif & Muneer, 2007; Kartal, 2022).

The oil and gas industry is exploring innovative and sustainable techniques to improve hydrocarbon recovery from carbonate reservoirs, which hold 60% of hydrocarbon reserves worldwide (Memon *et al.*, 2023a; Memon *et al.*, 2023b). Conventional methods are typically limited to low recovery rates of 30-35%, due to oil wetting characteristics in carbonate reservoirs. For optimal oil recovery, these reservoirs require an effective treatment to reverse their wetting condition from oil-wet to water-wet (Sagbana *et al.*, 2022). Recently, the Low-Salinity Waterflooding (LSWF) proved to be an effective alternative for enhancing oil recovery techniques in carbonate reservoirs. LSWF advances reservoir fluid displacement efficiency, enhancing hydrocarbon mobilisation for improving oil recovery in complex carbonate reservoirs, which provides a reliable energy supply (Malozyomov *et al.*, 2023; Nande & Patwardhan, 2022). The primary goal of the study is to alter their wetting conditions from oil-wet to water-wet by fluid-fluid and fluid-rock interactions. Nevertheless, much less attention is paid to the mechanisms involved, and the LSB compositions with chemical additives such as polymers and nanoparticles still remain unknown.

The initial wettability in carbonates prefers to be oil-wet due to the adsorption of polar compounds onto the carbonate surface, which decreases oil mobility through reservoir pores towards the producing wellbore (Deng *et al.*, 2024; Deng *et al.*, 2019; Mohammed *et al.*, 2015). Contact Angle (CA) measurement is the most frequent approach to govern the rock wetting conditions. A CA higher than 90° specifies oil-wet, while a CA with less than or equal to 90° reflects water-wet states (Isah *et al.*, 2023; Seyyedi *et al.*, 2015). Recently, the role of hybrid LSB solutions for wettability control has been investigated to improve oil displacement efficiency, a significant source of Enhanced Oil Recovery (EOR) in carbonates (Bolysbek *et al.*, 2024; Karimova *et al.*, 2023; Marquez *et al.*, 2025; Sagbana *et al.*, 2022).

Various factors for hybrid LSBs involved in the wettability alteration, including ionic composition, salinity concentrations, and chemical additives, influence oil recovery processes in carbonate reservoirs. These factors enhance the oil detachment process from the rock surface to transform into a hydrophilic state through wettability alteration. Further, the hybrid LSBs decrease the interfacial tension and viscosity due to the synergetic additives' effects, and enhance the oil recovery efficiency (Al-Busaidi *et al.*, 2023; Javadi & Fatemi, 2022; Marquez *et al.*, 2025; Nande & Patwardhan, 2022). However, the optimal concentration of hybrid LSBs and their performance under reservoir simulating conditions have not been explored. Likewise, the CA determination under different salinity environments and rising temperatures in carbonates remains limited in the literature.

This research explores the feasibility of designing hybrid LSB formulations using Chorgali

(CHG) carbonate core samples, Potwar Basin, Pakistan. The study aims to examine the mechanisms and chemical interactions of these hybrid LSBs that influence the reservoir rock wettability to become more hydrophilic. Subsequently, providing a sustainable approach to improve oil recovery technique in depleted reservoirs. This research combines different hybrid LSB injection schemes, such as a novel blend of reef salt, silica, and xanthan polymer, for better wettability adjustment effects and oil displacement efficiency in carbonate reservoirs.

The study employed CA experiments, which are the direct quantification of wettability shifts, and Fourier Transform Infrared (FTIR) to analyse mineralogical and functional group modifications during rock-brine interactions. The research proposes an innovative and sustainable approach to enhance oil recovery in mature carbonate reservoirs, addressing wettability issues, promoting integrated reservoir management, and next-generation EOR solutions.

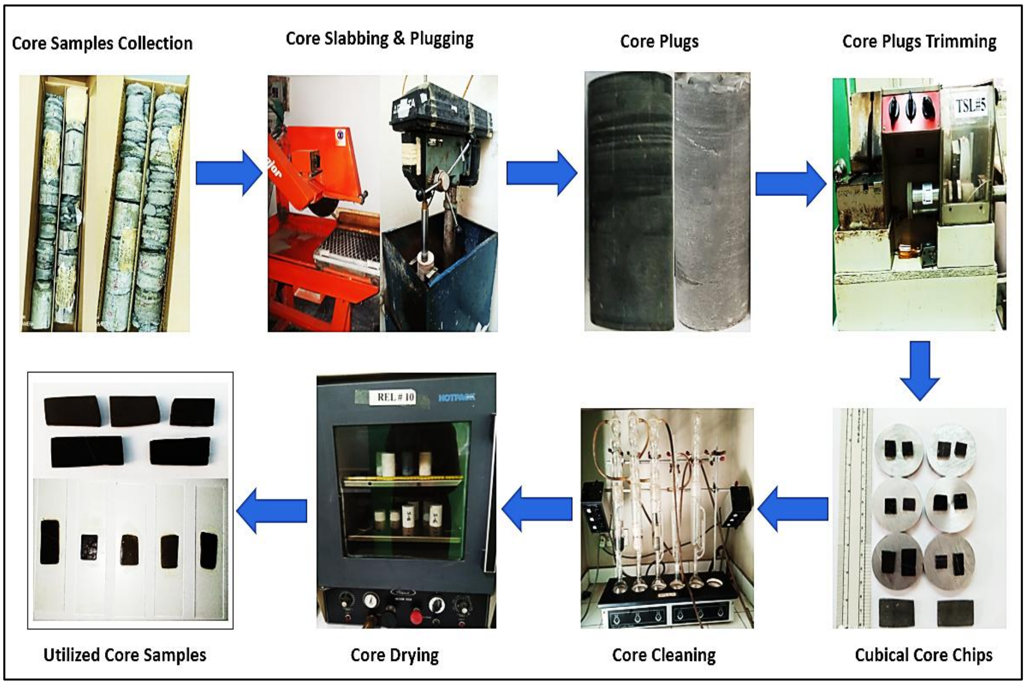
2. Materials utilised and preparation procedures

The study utilised the carbonate core samples, crude oil, and chemicals like different salts, xanthan polymer, and silica nanoparticles to formulate hybrid Low Saline Brines (LSB) for wettability alteration experiments. Each material employed in the study is described below.

2.1. Core samples collection and preparation

The study exploited reservoir cores from the Eocene carbonate Chorgali formation in the Indus Basin, Pakistan, collected from the subsurface Petcorelab, Hydrocarbon Development Institute of Pakistan (HDIP). These samples were prepared using standardised procedures and meticulously labelled and tagged for identification, as illustrated in Figure 1. The core plugs were cleaned with toluene using a Soxhlet extractor and dried in a hot oven at 70°C for 36 hours. Further, core cutting and trimming techniques were applied to get cubical core chips for ageing and wettability experiments.

Figure 1: Illustration of core preparation procedure



2.2. Crude oil

The study utilised the crude oil from a carbonate oil-producing field in Pakistan, collected under stock tank conditions with dead oil viscosity at 38.6°C and supplier-provided characteristics. These fundamental properties of the crude oil are crucial for fluid behaviour during wettability alteration experiments and are well represented in Table-1.

Table-1: Illustration of basic properties of crude oil utilised for the study

Properties	Units	Values	ASTM Method
Specific gravity 60/60°F	--	0.83	D-1298
API gravity 60/60°F	--	39.9	D-1299
Viscosity @ 60°C	Cp	1.16	D-446
Total Sulphur content	Wt%	1.1986	D-4294
BS & W	Vol%	0.1	D-4007
Water content D&S	Vol%	< 0.5	D-95

2.3. Chemicals utilised

The study utilised various chemicals to formulate hybrid low-salinity injection schemes for wettability alteration to improve residual oil recovery in carbonate reservoirs. The hybrid LSB contains key components like Sodium Chloride (NaCl), Calcium Chloride ($CaCl_2$), Potassium Chloride (KCl), Sodium Sulfate (Na_2SO_4), reef salt, xanthan polymer, and Silica (SiO_2) nanoparticles. The additives were strategically selected to enhance brine compositions and alter carbonate rock surface wettability. The chemicals were procured from China's Alpha Chemicals Pvt. Ltd. for high purity and experimental accuracy.

2.4. Preparation of hybrid LSB injection schemes

The study has developed five hybrid LSB injection schemes using salt compositions like NaCl, KCl, Na_2SO_4, and reef salt to assess the impact of ionic compositions on wettability alteration in carbonate reservoirs. Xanthan gum was added to increase brine viscosity and improve sweep efficiency. An innovative scheme combined SiO_2 nanoparticles with reef salt to study the fluid behaviour and brine-rock interactions. The low saline injection schemes involve precise weight percentages of salt compositions, sonication, distilled water, stirring, and xanthan polymer. The hybrid smart low-saline brine is prepared by thoroughly mixing the components and then drying them in a hot oven. The detailed properties of each hybrid injection scheme are provided in Table-2.

Table-2: Basic properties of hybrid low-saline injection schemes formulation.

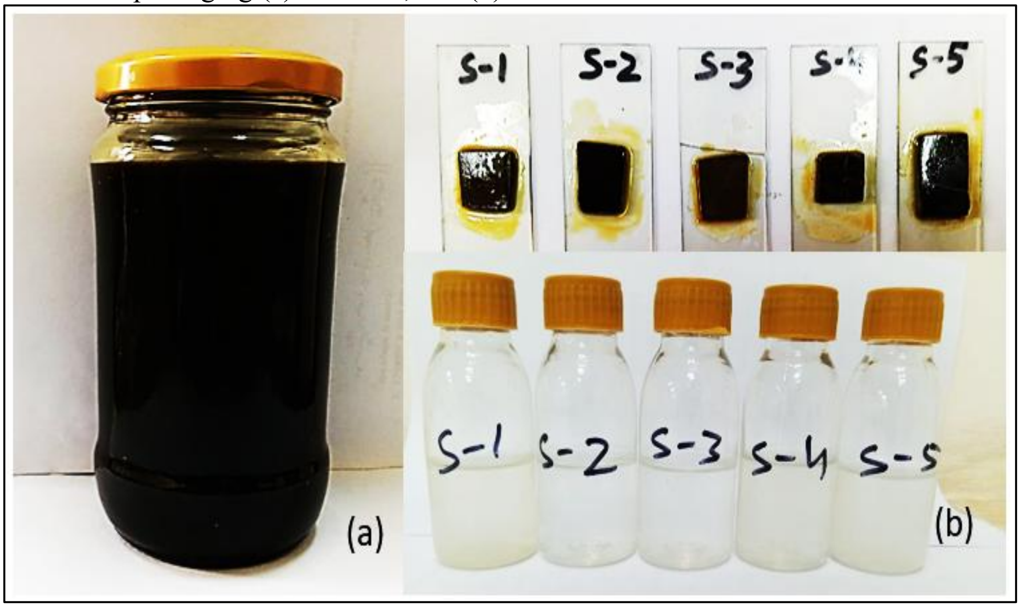
Sample ID	Salts	Concentration (ppm)	Density (gm/cc)	Viscosity (cp)
Scheme-1	NaCl + KCl + Na_2SO_4 + Xanthan Gum (Polymer)	2000	0.99408	1.21
Scheme-2	NaCl + KCl + Na_2SO_4 + Xanthan Gum (Polymer)	3000	0.99469	1.75
Scheme-3	NaCl + KCl +Na_2SO_4 + Xanthan Gum (Polymer)	4000	0.9951	1.481
Scheme-4	Reef Salt + Xanthan Gum (Polymer)	5000	0.9942	1.983
Scheme-5	Reef Salt + SiO_2 + Xanthan Gum (Polymer)	5000	0.9947	2.53673

3. Ageing of core samples

The core samples were aged in stearic acid solution (5mg/L) for seven days to replicate in-situ reservoir conditions and alter their surface wettability characteristics. Stearic acid-aged samples were then immersed in crude oil for three days, mimicking the interaction between carbonate cores and crude oil, allowing for realistic wettability changes. Subsequently, samples were aged into hybrid LSBs for seven days to evaluate wettability changes under different ionic conditions, as depicted in Figure-2.

The analysis was enriched by using varied low-salinity brine concentrations, providing insights into the impact of chemical compositions on wettability alteration. The carbonate substrates were heated at 40°C for 48 hours post-immersion to modify their surface properties, enhancing their representation of actual reservoir conditions.

Figure 2: Core samples aging (a) crude oil, and (b) low saline brines



4. Experimental program

The study assessed the efficiency of hybrid low salinity injection schemes for wettability alteration using a systematic approach and experimental procedures. The details of each analytical method employed in the study are given as follows:

4.1. Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR was utilised to verify the functional groups of hybrid low-saline injection formulations, detecting changes in mineral composition and structure, after salts were mixed with xanthan and silica nanoparticles. The ALPHA spectrometer from Bruker Optik GmbH was utilised to analyse brine formulations, revealing mineralogical shifts and molecular interactions, providing insights into their structural changes.

4.2. Contact Angle (CA) measurement

To analyse the rock/brine interactions, the CA of a liquid on a solid surface was determined using the sessile drop method. The method is commonly applied and involves placing a liquid droplet onto a rock surface to measure the rock surface wettability characteristics under controlled deposition. Further, the captive drop method was also employed to examine the wettability of oil droplets in hybrid low-salinity brines for rock/oil/brine interactions. It involves introducing an oil droplet into a brine-filled chamber, where the interaction between oil droplets and solid carbonate surfaces creates a CA, resembling dynamic reservoir environments.

5. Results and discussion

The results of each characterisation method employed in the study, and their impact on wettability alteration, are discussed as follows.

5.1. Basic properties of hybrid low-saline injection schemes

The study explores the development of hybrid Low Saline Brine (LSB) formulations, which demonstrate the impact of ionic composition and additives on brine effectiveness. These LSB injection schemes consist of primary salts such as NaCl, KCl, and Na_2SO_4, consistent with xanthan gum polymer for viscosity enhancement, as represented in Table-2.

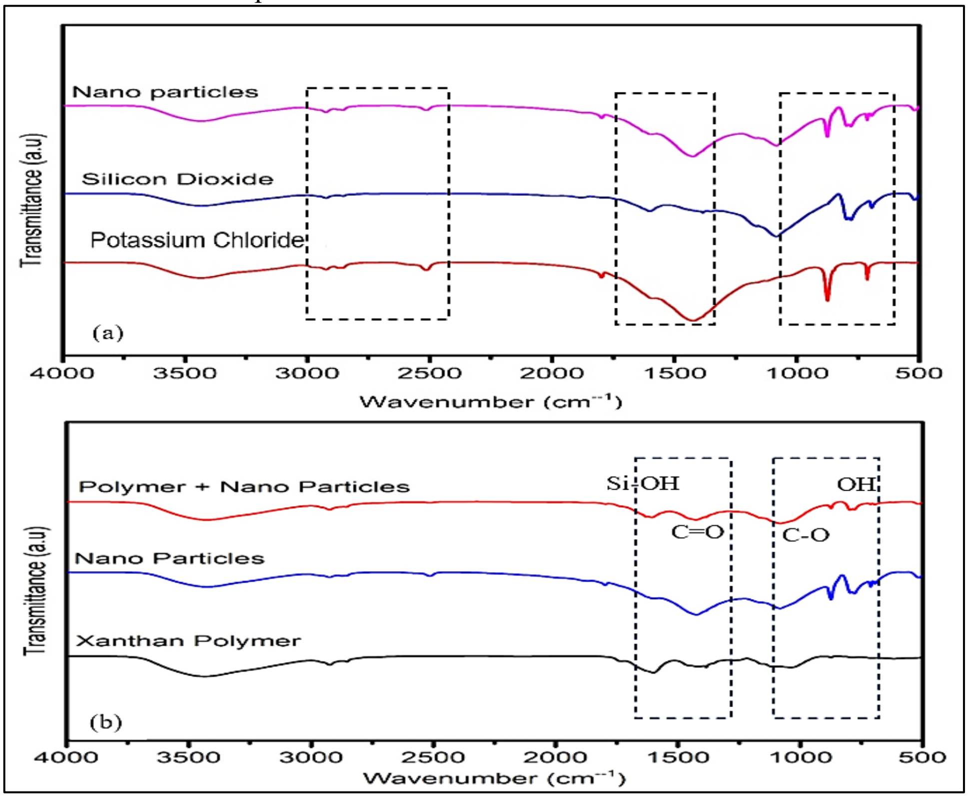
The basic properties, including density and viscosity, were determined using a hydrometer and a Sybolt viscometer at 60°C. Injection schemes 1-3 with increasing salt concentration show density around 0.9940 to 0.9951 g/cc, and viscosity ranges from 1.21 cp to 1.75 cp. Schemes 4 and 5 possess distinctive properties, with Scheme 4 combining reef salt and xanthan gum, achieving a viscosity of 1.983 cp. Whereas, Scheme-5 contains SiO_2 nanoparticles in addition to reef salt and xanthan polymer, representing the highest viscosity. This indicates the effectiveness of hybrid LSB formulations with improved fluid consistency and interfacial interaction potential, which is essential for enhancing oil displacement within carbonate formations.

5.2. Fourier Transform Infrared (FTIR) spectroscopy analysis of hybrid LS injection schemes

This study utilised FTIR spectroscopy to identify structural changes in low-saline injection schemes. The analysis aimed to confirm the integration of reef salt, xanthan polymer, and silica nanoparticles and analyse their molecular interactions to support wettability alteration in the carbonate reservoir. The results indicated the successful incorporation of salts in hybrid LSB injection schemes. The FTIR spectra of individual components like KCl and SiO_2 exposed sharp peaks at 800 cm^{-1}, 1100 cm^{-1}, 1400 cm^{-1}, and 2500 cm^{-1}, highlighted by rectangular boxes in Figure-3(a).

This corresponds to the presence and structural modifications of salts with nanoparticles due to their chemical functionalities with the polymer. In the xanthan and silica composite, the key absorption bands were observed at 850 cm^{-1}, 1550 cm^{-1}, and 1700 cm^{-1} peaks, as depicted in Figure-3(b). The 850 cm^{-1} band links to C-O-C stretching, indicating bonding with xanthan's carboxyl (C-O) and hydroxyl (OH) groups, which stabilise the composite to ensure its effective integration. The 1550 cm^{-1} peak is associated with the C=O stretching of xanthan's carboxylate groups, enhancing its stability in high-salinity environments. The 1700 cm^{-1} shift indicates bonding with silica's -Si-OH groups, supports the composite structure, improving viscosity and dispersion under reservoir conditions for EOR applications (Said *et al.*, 2021; Sarkar *et al.*, 2018).

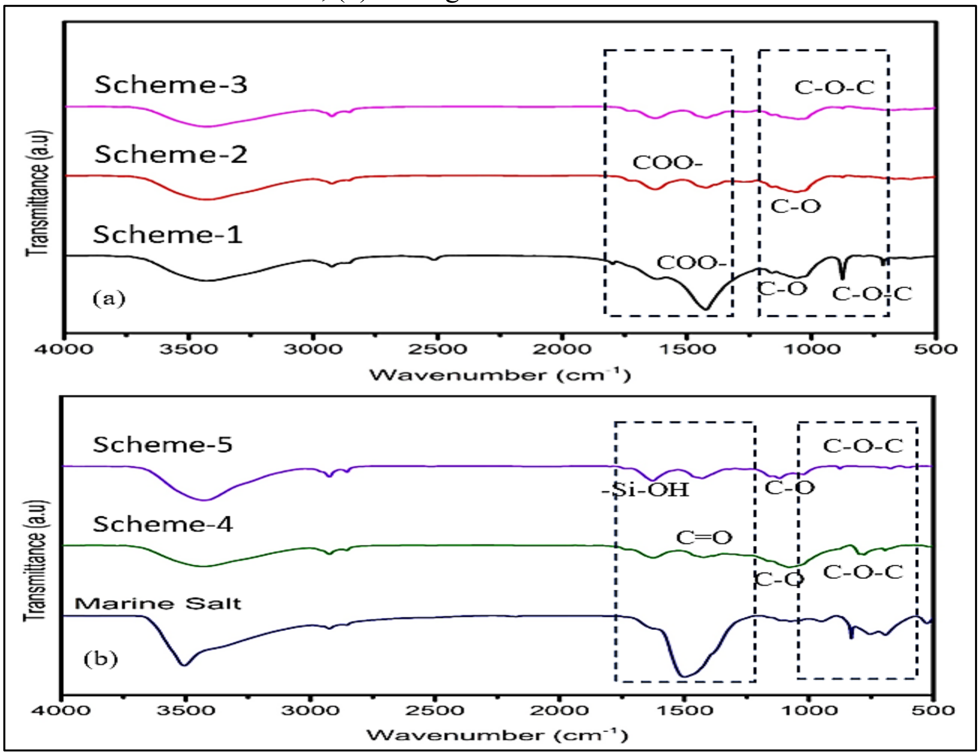
Figure 3: FTIR analysis of different salts (a) Calcium chloride, silica particles and their composite form, (b) Nanoparticles and their composite form



The FTIR analysis of injection Scheme 1 indicates several spectral bands at 850 cm⁻¹, 1100 cm⁻¹, and 1400 cm⁻¹, validating proper mixing of xanthan polymer with KCL salt, as shown in Figure-4(a). These peaks are attributed to C-O-C stretching, including C-O and COO- stretching of hydroxyl and carboxylate groups, respectively. Subsequently, the shifts indicate the xanthan compatibility with divalent ions (K^+) to enhance the wettability alteration capabilities of the solution (Cai *et al.*, 2020; Liu *et al.*, 2021; Nsengiyumva & Alexandridis, 2022). Likewise, Schemes 2 and 3 showed significant spectral changes, signifying effective interaction between salts and the polymer matrix. Furthermore, the study involved reef salt (marine salt), xanthan polymer, and SiO_2 nanoparticles in Schemes 4 and 5, confirming the successful formulations in achieving structural modifications, as shown in Figure-4(b).

The FTIR analysis reveals the distinct peaks at 850 cm^{-1}, 1200 cm^{-1}, 1450 cm^{-1}, and 1650 cm^{-1}. These peaks correspond to specific functional groups in xanthan and similar polymer composites. The peak 850 cm^{-1} is associated with C-O-C stretching, indicating xanthan glycosidic linkage to signify the polysaccharide stability and successful integration of additives with nanoparticles. 1200 cm^{-1} peak is attributed to C-O stretching in hydroxyl groups in the formulation. Although the band at 1450 cm^{-1} is correlated to C=O stretching in the carboxylate group, demonstrating the stability of the reef salt in formulation. Similarly, the 1650 cm^{-1} peak indicates a silicate hydroxyl (-Si-OH) group shift, supporting the composite structure for EOR applications. This shifting of various functional groups in the formulation structure is vital for developing ion-exchange relations for chemical stability and enhancing wettability alteration mechanisms. The results are aligned and supportive with previous studies emphasising the role of FTIR in tracking chemical alterations within injection fluids (Abbas *et al.*, 2023; Nowrouzi *et al.*, 2020; Sanyal *et al.*, 2017).

Figure 4: FTIR analysis showing structural changes indicated by rectangular boxes, (a) representing the mixing of schemes -01 to scheme-03, (b) mixing of scheme-04 and scheme-05 with marine salt

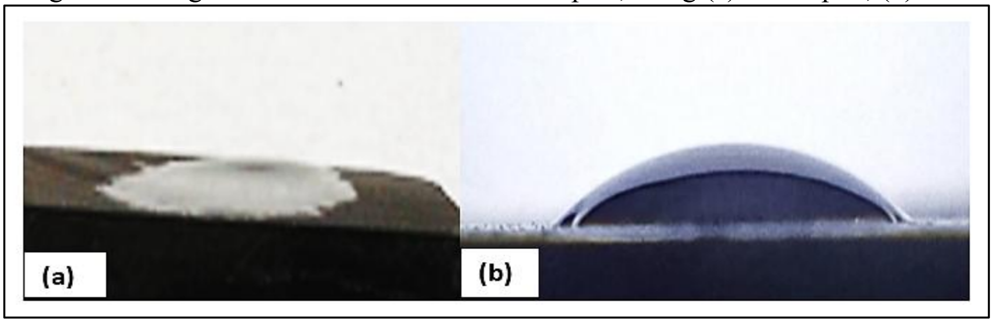


The study validates the effective integration of hybrid LSB schemes through the shifting of functional groups between formulation components. This shifting develops the ionic and molecular interactions to improve composite stability for substantial rock-brine interactions and promotes wettability alteration mechanisms (Jang *et al.*, 2018; Rostami *et al.*, 2020). The FTIR analysis confirms the successful formulation of LSB schemes, which supports the theoretical framework for evaluating the injection fluid performance.

5.3. Impact of oil/rock/air interaction on wettability (original wettability determination)

To investigate the effect of oil-rock-air interactions, two CA tests were performed by placing crude oil and water droplets on separate unaged and uncleaned cores to evaluate their initial wettability. Crude oil rapidly imbibed into one sample, while water formed a definite droplet shape on another sample, as shown in Figure-5. This indicates the initial oil wettability state of the examined core samples, reflecting strong oil-rock attraction due to their original surface chemistry and mineralogical properties (Deng *et al.*, 2024; Saputra *et al.*, 2021). The definite CA by water droplet further confirmed the non-water-wet conditions, attributed to the formation of a hydrophobic layer on carbonate cores due to the adsorption of polar organic compounds (Noruzi *et al.*, 2024; Singh *et al.*, 2016). These results highlighted the initial oil wetting characteristics of the core samples, which hinder the water-based oil displacement, making recovery more difficult. The finite water CA confirms these characteristics, suggesting partial water spreading but insufficient wettability alteration for oil displacement (Saputra *et al.*, 2021). Oil-wet systems tend to imbibe oil into pore spaces, reducing water-based displacement mechanisms, subsequently posing significant challenges for EOR. To counteract this issue, accurate contact angle measurement necessitates effective EOR strategies like LSWF and chemical additives to modify the original wettability and improve recovery efficiency (Al-Yaseri *et al.*, 2016; Bolysbek *et al.*, 2024). Thus, these findings emphasise the implication of integrating advanced EOR techniques with precise wettability alteration for substantial recovery improvements.

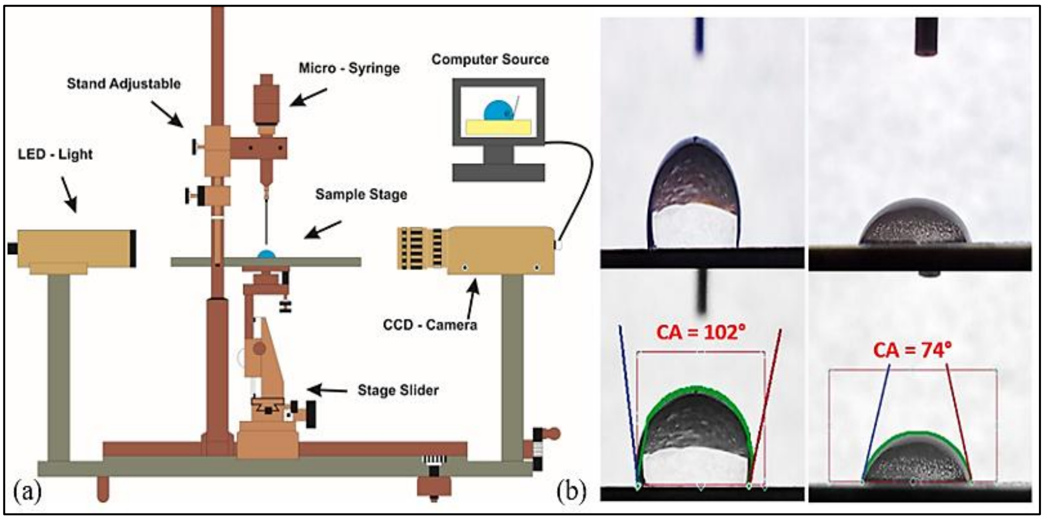
Figure 5: Original wetting condition of the carbonate samples, using (a) oil droplet, (b) water droplet



5.4. Effects of brine salinity on contact angle measurement (rock/air/brine interactions)

The CA measurement of carbonate core samples (Chorgali Formation) under rock/air/brine interactions was evaluated using the sessile (pendant drop) method at different brine concentrations (0.1M, 0.2M, 0.3M, and 0.4M). The sessile drop method is a non-destructive technique used to determine the contact angle between a liquid droplet and a solid surface, substantial for EOR implications. The CA measurements under specific conditions were evaluated using Ossila software, recognising the carbonate wetting behaviour. The schematic setup and the examined drop shapes are displayed in Figure-6, while CA results for stearic acid-treatment at various brine salinities are represented in Table-3. The finding revealed that results CA decrease with increasing brine concentration, indicating a shift from hydrophobic to water-wet conditions. Sample CHG-01 shows a significant change in wettability, dropping from 126° at 0.1 M NaCl to 80° at 0.4 M NaCl concentration. This trend is consistent across most of the samples, despite some deviations in sample CHG-04, indicating that higher brine salinity encourages the water-wet behaviour, and promotes oil displacement (Javadi & Fatemi, 2022).

Figure 6: (a) Contact angle set-up schematic diagram, (b) Developed platform utilised for the sessile drop method

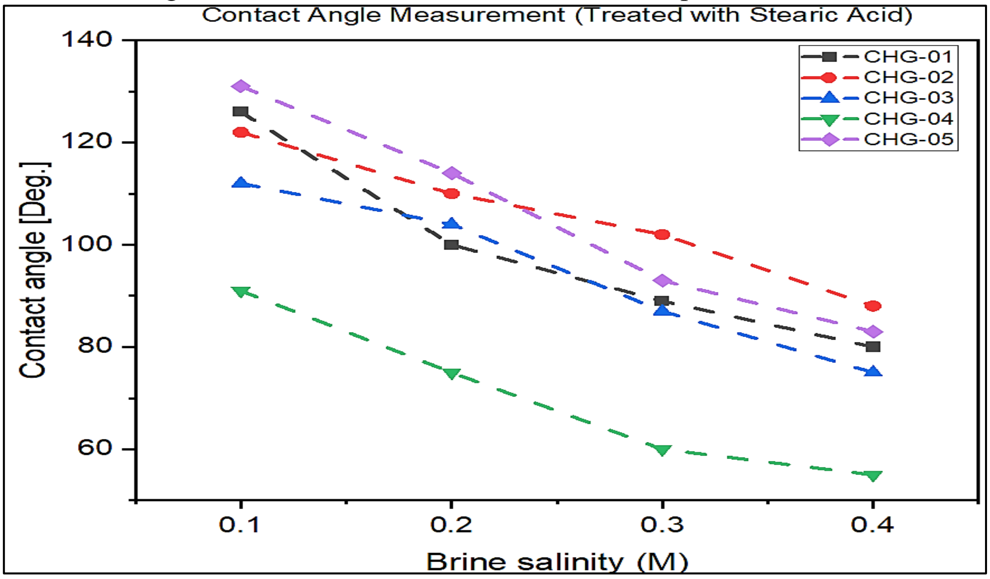


The study found that most samples show hydrophobic or oil-wet behaviour, with CA greater than 90° indicating strong oil affinity. This is a reliable criterion for determining surface wettability, with angles above 90° indicating hydrophobicity and angles below 90° signifying hydrophilicity (Al-Busaidi *et al.*, 2023; Deng *et al.*, 2019). However, sample CHG-04 showed significant deviation, possibly due to higher clay or quartz content, as depicted in Figure-7. It is because the Stearic acid treatment does not significantly alter the wettability of clay-rich samples, aligning with CHG-04's unique behaviour (Al-Shalabi & Sepehrnoori, 2016; Al-Shirawi *et al.*, 2021). The findings revealed that increasing NaCl brine concentration from 0.1M to 0.4M led to a decrease in CA due to the salting-out effect. This phenomenon reduces the stearic acid solubility on carbonate surfaces, shifting wettability towards more water-wet conditions (Al-Shalabi & Sepehrnoori, 2016; Aslan *et al.*, 2016; Nande & Patwardhan, 2022), signifying the impact of brine salinity on wettability alteration (Deng *et al.*, 2019). The salinity adjustment further improves the electrostatic interactions at the rock-brine interface, increasing water affinity by reducing oil molecule adhesion (Javadi & Fatemi, 2022). Subsequently, enhance oil displacement and recovery efficiency in carbonate reservoirs (Deng *et al.*, 2019; Nande & Patwardhan, 2022). This study underlines the importance of salinity in optimising wettability alteration mechanisms and emphasises the need for tailored brine formulations for effective EOR techniques.

Table-3: Contact angle (average) measured under different brine concentrations for carbonate core samples treated with stearic acid

Sample ID	NaCl Brine Salinities							
	0.1 M		0.2 M		0.3 M		0.4 M	
	Avg. CA Deg.	RMS Error	Avg. CA Deg.	RMS Error	Avg. CA Deg.	RMS Error	Avg. CA Deg.	RMS Error
CHG - 01	126°	± 1.77	100°	± 1.35	89°	± 0.53	80°	± 1.22
CHG – 02	120°	± 0.37	102°	± 0.54	98°	± 0.56	88°	± 0.57
CHG – 03	111°	± 1.48	104°	± 1.63	87°	± 0.43	75°	± 1.36
CHG - 04	74°	± 0.35	70°	± 0.54	60°	± 0.46	50°	± 0.67
CHG - 05	131°	± 0.47	118°	± 0.37	93°	± 0.65	73°	± 0.55

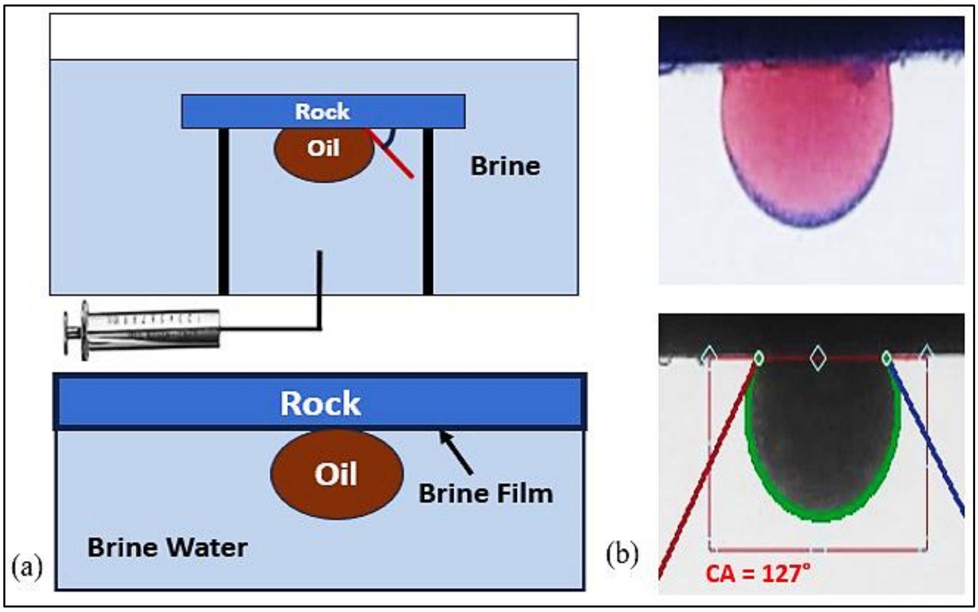
Figure 7: Contact angle measurement of stearic acid-treated samples at various brine concentrations



5.5. Effects of hybrid low-saline brines and temperature on contact angle measurement (rock/oil/brine interactions)

The impact of hybrid LSB formulations on the oil wettability behaviour of the carbonate cores was examined through the captive drop method under varying temperature conditions. Since wettability directly influences fluid movement and distribution within porous rocks, affecting oil recovery efficiency (Deng *et al.*, 2021). Lower CA reflects water-wet behaviour, while higher angles suggest hydrophobic or oil-wet conditions (Deng *et al.*, 2019; Deng *et al.*, 2021). Initially, the carbonate cores were aged into different hybrid LSB schemes, and the CA of an oil droplet was determined for wettability changes in a controlled low salinity environment. The analysis illustrates the dynamic relationship between contact angle changes and surface wettability within carbonate substrates for different LSB schemes. The results are summarised in Table-4, as depicted in Figure and Figure-9 demonstrate that both brine composition and temperature have a significant effect on CA behaviour.

Figure 8: (a) Representing the developed captive drop method tool, (b) schematic diagram of the captive drop method for oil/rock/brine CA measurement



As temperatures increased from 25°C to 60°C, the contact angle consistently decreased across all hybrid schemes, indicating a transition to more water-wet conditions. For scheme 01, the CA decreased from 126° at 25°C to 101° at 60°C, as shown in Figure-9. In contrast, Scheme 04 showed a similar trend with CA dropping from 118° at 25°C to 99° at 60°C, indicating a stronger tendency towards water-wet behaviour. The most considerable decline was observed in Scheme 05, where CA reduced from 149° to 111°, signifying the temperature effects on oil wettability.

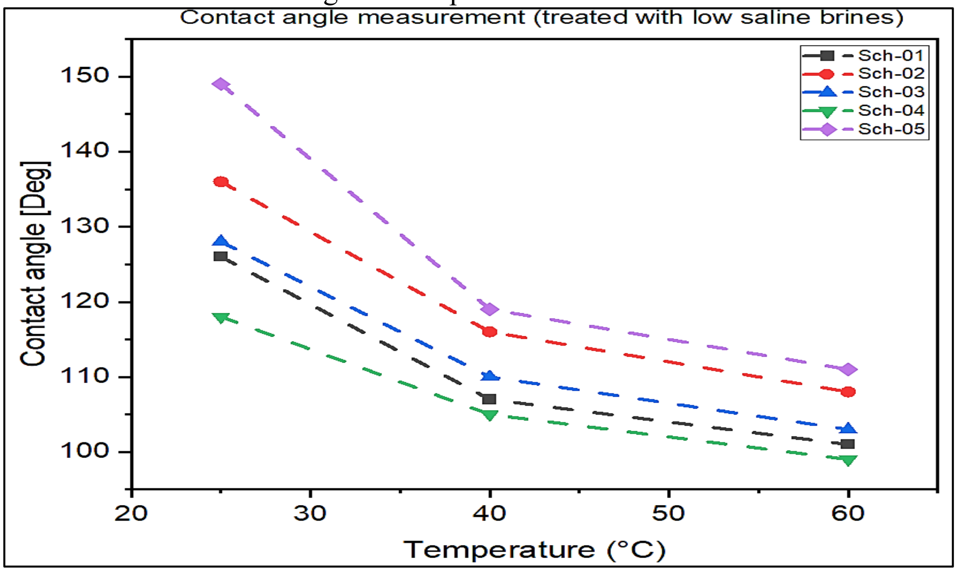
The findings reveal that designed hybrid schemes are more reactive to wettability alteration at increasing temperatures, specifically scheme 05, which reduces the CA by 30° at 60°C. This alteration supports the hydrophilic state in carbonates to improve reservoir fluid mobility and reduce residual oil saturation (Javadi & Fatemi, 2022; Mohammadi *et al.*, 2019). The performance of these hybrid schemes is attributed to the synergetic effect of reef salt, xanthan polymer, and silica particles, making them substantial for enhanced oil recovery (Liu & Wang, 2020; Mahani *et al.*, 2017). The xanthan provides brine stability and viscosity in high-temperature conditions (Hassan *et al.*, 2022), while silica nanoparticles enhance fluid rock interactions through surface bonding with carbonate minerals (Jang *et al.*, 2018). This combination leads to stronger ionic interaction, better brine dispersion, and a uniform decrease in CA across the temperature ranges (Javadi & Fatemi, 2022).

The experimental trends highlighted the oil wetting characteristics of the examined samples at lower temperatures, but higher temperatures transformed their wettability toward more wet conditions. The elevated temperatures lead to a drop in CA below 90°, enhancing rock-brine interactions to promote oil displacement efficiency for EOR. The results are aligned with previous studies confirming the relationship between temperature and wettability shifts in carbonates (Bashir *et al.*, 2022; Dehaghani & Badizad, 2019; Mahani *et al.*, 2017; Shar *et al.*, 2023). The study found that hybrid LSB formulations and temperature significantly influence wettability, enhancing oil displacement efficiency, thereby facilitating effective EOR strategies for maximum oil recovery in carbonates.

Table-4: Contact angle (average) measured under different temperature conditions after ageing in low saline injection schemes

Sample ID	Temperature °C					
	25		40		60	
	Avg. CA Deg.	Avg. RMS Error	Avg. CA Deg.	Avg. RMS Error	Avg. CA Deg.	Avg. RMS Error
Scheme 01	127°	± 0.40	107°	± 0.41	101°	± 0.44
Scheme 02	136°	± 0.53	116°	± 0.47	108°	± 0.34
Scheme 03	128°	± 0.46	110°	± 0.39	103°	± 0.52
Scheme 04	118°	± 0.37	105°	± 0.40	99°	± 0.33
Scheme 05	149°	± 0.64	119°	± 0.49	111°	± 0.38

Figure 9: Relation between contact angle Vs temperature

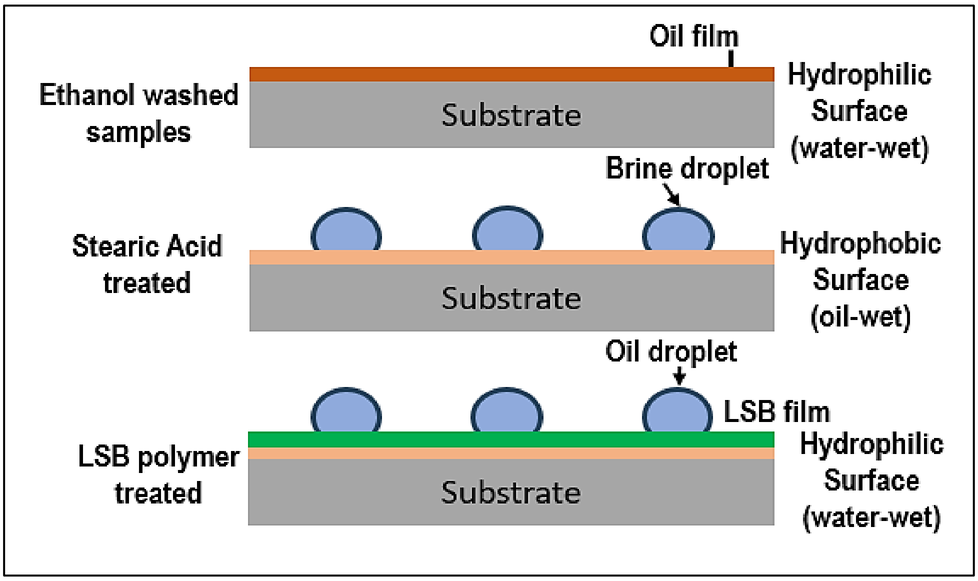


5.6. Surface treatment and mechanisms involved in wettability alteration

The surface treatment and wettability alteration are essential for improving oil recovery efficiency in carbonate reservoirs. Treatments like ethanol washing, stearic acid application, and low-salinity brine polymer formulations alter the carbonate surface properties and improve hydrophilicity, as shown in Figure . Initially, ethanol washing was applied to remove hydrocarbon residues and impurities from the carbonate cores, revealing its hydrophilic properties. This results in water-wet conditions and supports wettability modification. Subsequently, the carbonate cores become hydrophobic and oil-wet when treated with stearic acid, replicating in-situ reservoir environments where hydrocarbons adhere to rock due to electrostatic attraction. This presents a challenge for recovery as oil droplets bind tightly to the rock, resisting displacement. Similarly, hybrid LSB formulations were employed containing xanthan gum, silica nanoparticles, and reef salt components like Na^+, K^+, and SO_4^{2-} to alter wettability at rock-fluid interfaces (de Aguiar *et al.*, 2021; Khoramian *et al.*, 2024; Nande & Patwardhan, 2022). The ions from reef salt modify electrostatic forces, promoting a shift from oil-wet to water-wet conditions through electrical double layer expansion, polar oil molecules displacement and oil detachment mechanisms (Li & Zhang, 2018). The silica nanoparticles increase carbonate surface hydrophilicity through fluid-rock interactions (Lashari *et al.*, 2022), while, xanthan polymer improves brine mobility and efficiency during waterflooding operations (de Aguiar *et al.*, 2021).

During Low-Salinity Waterflooding (LSWF), the wettability alteration is mainly influenced by mechanisms including surface charge dynamics, ionic compositions, and electrical charge modifications at rock-fluid interface. Similarly, the factors like temperature, ionic strength, and polymer formulations further enhance the effect (Purswani *et al.*, 2017; Sagbana *et al.*, 2022). The specific ions in hybrid LSBs compositions expand the electrical double layer mechanism, reducing attractive forces between oil and rock minerals, reduces interfacial tension to displace oil molecules more easily (Maya *et al.*, 2023). Moreover, higher temperatures increase the ionic mobility, boosting the rock hydrophilic conditions and making them more water wet for improving recovery efficiency (Deng *et al.*, 2021; Mahani *et al.*, 2017). The findings reveal that hybrid LSB formulations play a vital role in shifting carbonate wettability by various specified mechanisms, as shown in Figure This study validates a conceptual thoughtful of the mechanisms involved in wettability shift, based on aligned literature. The addition of xanthan and silica nanoparticles enhances the LSB potential, making it suitable for challenging carbonate reservoir conditions.

Figure 10: Schematic diagram showing effect of surface treatment on wetting classification of carbonate substrate



6. Conclusions

This study investigates the effects of hybrid low-saline injection schemes for wettability alteration in carbonate cores for EOR implications. The conclusions drawn are that hybrid low-saline brine formulations significantly modify the carbonate wettability to promote oil displacement efficiency. The designed hybrid brine compositions, specifically containing reef salt, silica nanoparticles, and xanthan gum, substantially shifted the rock surface from oil-wet to water-wet conditions. The elevated temperatures and adjusted brine salinity further enhance this effect for improving oil recovery. Among all hybrid compositions, scheme-05 emerged as the most effective formulation, which incorporated silica nanoparticles with xanthan polymer, demonstrating the improved wettability adjustment. This performance is due to the nanoparticle adsorption on the carbonate surface and surface charge modifications, which promote the hydrophilic behaviour. Likewise, certain ions from reef salt, like Ca^{2+}, K^{+} and SO_4^{2-}, signified the multicomponent ion exchange, enabling polar oil components to detach from carbonate surfaces for oil displacement. The findings confirm the potential of hybrid LSB formulations to overcome wettability issues in carbonate reservoirs. It also provides valuable insights into the mechanisms of wettability alteration and highlights the effectiveness of combining brine salinity, polymers, and nanoparticles in improving oil displacement. The study underlines the practical implications of the hybrid LS brine formulations in promoting a hydrophilic state, thereby enhancing the hydrocarbon recovery process in carbonate reservoirs.

Declaration of conflict of interest

The author(s) declared no potential conflicts of interest(s) with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) received no financial support for the research, authorship and/or publication of this article.

ORCID iD:

Faisal Hussain Memon https://orcid.org/0009-0008-4024-3185

Ghulam Abbas https://orcid.org/0009-0008-6625-9249

Tahir Ali Soomro https://orcid.org/0009-0000-8285-981X

Abdul Haque Tunio https://orcid.org/0009-0009-8196-7654

Publisher's Note

IDEA Publishers Group (AJSET IDEA-PG) stands neutral with regard to the jurisdictional claims in the published maps and the institutional affiliations.

References

Abbas, G., Tunio, A. H., Memon, K. R., Mahesar, A. A., Memon, F. H., & Abbasi, G. R. (2023). Modification of cellulose ether with organic carbonate for enhanced thermal and rheological properties: Characterization and analysis. *ACS Omega, 8*(28), 25453–25466. https://doi.org/10.1021/acsomega.3c02974

Al-Busaidi, K. K., Souayeh, M., Al-Maamari, R. S., Al-Busaidi, I. K., & Divers, T. (2023). Experimental investigation of wettability alteration of oil-wet carbonate surfaces using engineered polymer solutions: The effect of potential determining ions ([Mg2+/SO42−], and [Ca2+/SO42−] ratios). *Geoenergy Science and Engineering, 230*, 212182. https://doi.org/10.1016/j.geoen.2023.212182

Al-Shalabi, E. W., & Sepehrnoori, K. (2016). A comprehensive review of low salinity/engineered water injections and their applications in sandstone and carbonate rocks. *Journal of Petroleum Science and Engineering, 139*, 137–161. https://doi.org/10.1016/j.petrol.2015.11.027

Al-Shirawi, M., Karimi, M., & Al-Maamari, R. S. (2021). Impact of carbonate surface mineralogy on wettability alteration using stearic acid. *Journal of Petroleum Science and Engineering*, *203*, 108674. https://doi.org/10.1016/j.petrol.2021.108674

Al-Yaseri, A. Z., Lebedev, M., Barifcani, A., & Iglauer, S. (2016). Receding and advancing (CO2+ brine+ quartz) contact angles as a function of pressure, temperature, surface roughness, salt type and salinity. *The Journal of Chemical Thermodynamics, 93*, 416–423. https://doi.org/10.1016/j.jct.2015.07.031

Asif, M., & Muneer, T. (2007). Energy supply, its demand and security issues for developed and emerging economies. *Renewable and Sustainable Energy Reviews, 11*(7), 1388–1413. https://doi.org/10.1016/j.rser.2005.12.004

Aslan, S., Najafabadi, N. F., Firoozabadi, A. (2016). Non-monotonicity of the contact angle from NaCl and MgCl2 concentrations in two petroleum fluids on atomistically smooth surfaces. *Energy & Fuels, 30*(4), 2858–2864. https://doi.org/10.1021/acs.energyfuels.6b00175

Bashir, A., Haddad, A. S., & Rafati, R. (2022). A review of fluid displacement mechanisms in surfactant-based chemical enhanced oil recovery processes: Analyses of key influencing factors. *Petroleum Science, 19*(3), 1211–1235. https://doi.org/10.1016/j.petsci.2021.11.021

Bolysbek, D., Uzbekaliyev, K., & Assilbekov, B. J. (2024). Rock wettability alteration induced by the injection of various fluids: a review. *Applied Sciences, 14*(19), 8663. https://doi.org/10.3390/app14198663

Cai, X., Du, X., Zhu, G., & Cao, C. (2020). Induction effect of NaCl on the formation and stability of emulsions stabilized by carboxymethyl starch/xanthan gum combinations. *Food Hydrocolloids, 105*, 105776. https://doi.org/10.1016/j.foodhyd.2020.105776 de Aguiar, K. L. N. P., Palermo, L. C. M., & Mansur, C. R. E. (2021). Polymer viscosifier systems with potential application for enhanced oil recovery: a review. *Oil & Gas Science and Technology - Rev. IFP Energies nouvelles 76*, 65. https://doi.org/10.2516/ogst/2021044

Dehaghani, A. H. S., & Badizad, M. H. (2019). Impact of ionic composition on modulating wetting preference of calcite surface: Implication for chemically tuned water flooding. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 568*, 470–480. https://doi.org/10.1016/j.colsurfa.2019.02.009

Deng, X., Bashir, A., Kamal, M. S., Raza, A., Patil, S., Zhou, X.,…Shakil Hussain, S. M. J. A. o. (2024). Insights into rock wettability influencing factors: a review. *ACS Omega, 9*(50), 48899–48917. https://doi.org/10.1021/acsomega.4c07387

Deng, X., Kamal, M. S., Patil, S., Hussain, S. M. S., & Zhou, X. (2019). A review on wettability alteration in carbonate rocks: wettability modifiers. *Energy & Fuels, 34*(1), 31–54. https://doi.org/10.1021/acs.energyfuels.9b03409

Deng, X., Tariq, Z., Murtaza, M., Patil, S., Mahmoud, M., & Kamal, M. S. (2021). Relative contribution of wettability Alteration and interfacial tension reduction in EOR: A critical review. *Journal of Molecular Liquids, 325*, 115175. https://doi.org/10.1016/j.molliq.2020.115175

Hassan, A. M., Al-Shalabi, E. W., & Ayoub, M. A. (2022). Updated perceptions on polymer-based enhanced oil recovery toward high-temperature high-salinity tolerance for successful field applications in carbonate reservoirs. *Polymers, 14*(10), 2001. https://doi.org/10.3390/polym14102001

Isah, A., Arif, M., Mahmoud, M., & Kamal, M. S. (2023). Influence of rock permeability and surface conditioning on carbonate wettability: A link between contact angle and Amott-index. *Geoenergy Science and Engineering, 227*, 211892. https://doi.org/10.1016/j.geoen.2023.211892

Jang, H., Lee, W., & Lee, J. (2018). Nanoparticle dispersion with surface-modified silica nanoparticles and its effect on the wettability alteration of carbonate rocks. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 554*, 261–271. https://doi.org/10.1016/j.colsurfa.2018.06.045

Javadi, A. H., & Fatemi, M. J. F. (2022). Impact of salinity on fluid/fluid and rock/fluid interactions in enhanced oil recovery by hybrid low salinity water and surfactant flooding from fractured porous media. *329*, 125426. https://doi.org/10.1016/j.fuel.2022.125426

Karimova, M., Kashiri, R., Pourafshary, P., & Hazlett, R. (2023). A review of wettability alteration by spontaneous imbibition using low-salinity water in naturally fractured reservoirs. *Energies, 16*(5), 2373. https://doi.org/10.3390/en16052373

Kartal, M. T. (2022). The role of consumption of energy, fossil sources, nuclear energy, and renewable energy on environmental degradation in top-five carbon producing countries. *Renewable Energy, 184*, 871–880. https://doi.org/10.1016/j.renene.2021.12.022

Khoramian, R., Issakhov, M., Pourafshary, P., Gabdullin, M., & Sharipova, A. (2024). Surface modification of nanoparticles for enhanced applicability of nanofluids in harsh reservoir conditions: a comprehensive review for improved oil recovery. *Advances in Colloid and Interface Science, 333*, 103296. https://doi.org/10.1016/j.cis.2024.103296

Lashari, N., Ganat, T., Elraies, K. A., Ayoub, M. A., Kalam, S., Chandio, T. A., Qureshi, S., & Sharma, T. (2022). Impact of nanoparticles stability on rheology, interfacial tension, and wettability in chemical enhanced oil recovery: a critical parametric review. *Journal of Petroleum Science and Engineering, 212*, 110199. https://doi.org/10.1016/j.petrol.2022.110199

Li, Z., & Zhang, P. (2018). Influence of Multicomponent Ion Exchange and Brine Chemistry on Wettability Alteration in Carbonate Reservoirs. *SPE Reservoir Evaluation & Engineering*, *21*(4), 888-899.

Liu, F., & Wang, M. (2020). Review of low salinity waterflooding mechanisms: wettability alteration and its impact on oil recovery. *Fuel, 267*, 117112. https://doi.org/10.1016/j.fuel.2020.117112

Liu, H., Wu, J., Zhang, Y., Wang, W., Chen, Y., & Lang, Q. (2021). Rheological properties of xanthan gum and polyacrylamide mixture in inorganic salt solutions. *International Journal of Heat and Technology, 39*(4), 1358–1364. https://doi.org/10.18280/ijht.390436

Mahani, H., Menezes, R., Berg, S., Fadili, A., Nasralla, R., & Voskov, D. (2017). Insights into the impact of temperature on the wettability alteration by low salinity in carbonate rocks. *Energy & Fuels, 31*(8), 7839–7853. https://doi.org/10.1021/acs.energyfuels.7b00776

Majeed, A., & Mahesar, A. (2016, December 6). Pakistan's Kirthar fold belt tight gas reservoirs show development potential. *Oil and Gas Journal*.

Malozyomov, B. V., Martyushev, N. V., Kukartsev, V. V., Tynchenko, V. S., Bukhtoyarov, V. V., Wu, X.,…Kukartsev, V. A. (2023). Overview of methods for enhanced oil recovery from conventional and unconventional reservoirs. *16*(13), 4907. https://doi.org/10.3390/en16134907

Marquez, R., Ding, H., Barrios, N., Vera, R. E., Salager, J.-L., Al-Shalabi, E. W. (2025). Recent advances in enhanced oil recovery with low-salinity waterflooding and its hybrid methods in carbonate reservoirs. https://doi.org/10.1021/acs.energyfuels.4c06023

Maya, G., Carreño Otero, A. L., Monares Bueno, F. L., Romero Bohórquez, A. R., Cortés, F. B., Franco, C. A., & Manrique, E. (2023). Rock–oil–brine dominant mechanisms in smart water flooding. *Energies, 16*(4), 2043. https://doi.org/10.3390/en16042043

Memon, F. H., Tunio, A. H., Mahesar, A. A., & Abbas, G. (2023a). Integrated Study to Assess the Diagenetic Impacts on Petro-Physical Characteristics and Reservoir Quality of Sukkur Rift Zone. *19*(ISSUE 02 FEBRUARY 2023), 1858–1865. http://xisdxjxsu.asia

Memon, F. H., Tunio, A. H., Memon, K. R., Mahesar, A. A., & Abbas, G. J. M. (2023b). Unveiling the diagenetic and mineralogical impact on the carbonate formation of the Indus Basin, Pakistan: implications for reservoir characterisation and quality assessment. *13*(12), 1474. https://doi.org/10.3390/min13121474

Mohammadi, S., Kord, S., & Moghadasi, J. (2019). The hybrid impact of modified low salinity water and anionic surfactant on oil expulsion from carbonate rocks: a dynamic approach. *Journal of Molecular Liquids, 281*, 352–364. https://doi.org/10.1016/j.molliq.2019.02.092

Mohammed, M., & Babadagli, T. (2015). Wettability alteration: A comprehensive review of materials/methods and testing the selected ones on heavy-oil containing oil-wet systems. *Advances in Colloid and Interface Science, 220*, 54–77. https://doi.org/10.1016/j.cis.2015.02.006

Nande, S. B., & Patwardhan, S. D. (2022). A review on low salinity waterflooding in carbonates: challenges and future perspective. *Journal of Petroleum Exploration and Production Technology, 12*(4), 1037–1055. https://doi.org/10.1007/s13202-021-01361-5

Noruzi, Y., Sharifi, M., Fahimpour, J., Sabet, M., Akbari, M., & Hosseini, S. (2024). The state-of-the-art of wettability alteration in sandstones and carbonates: A mechanistic review. *Fuel, 356*, 129570. https://doi.org/10.1016/j.fuel.2023.129570

Nowrouzi, I., Manshad, A. K., & Mohammadi, A. H. (2020). Effects of Tragacanth Gum as a natural polymeric surfactant and soluble ions on chemical smart water injection into oil reservoirs. *Journal of Molecular Structure, 1200*, 127078. https://doi.org/10.1016/j.molstruc.2019.127078

Nsengiyumva, E. M., & Alexandridis, P. (2022). Xanthan gum in aqueous solutions: Fundamentals and applications. *International Journal of Biological Macromolecules, 216*, 583–604. https://doi.org/10.1016/j.ijbiomac.2022.06.189

Purswani, P., Tawfik, M. S., Karpyn, Z. T. (2017). Factors and mechanisms governing wettability alteration by chemically tuned waterflooding: a review. *Energy & Fuels, 31*(8), 7734–7745. https://doi.org/10.1021/acs.energyfuels.7b01067

Rostami, P., Sharifi, M., Aminshahidy, B., & Fahimpour, J. (2020). Enhanced oil recovery using silica nanoparticles in the presence of salts for wettability alteration. *Journal of Dispersion Science and Technology, 41*(3), 402–413 https://doi.org/10.1080/01932691.2019.1583575

Sagbana, P. I., Sarkodie, K., & Nkrumah, W. A. (2022). A critical review of carbonate reservoir wettability modification during low salinity waterflooding. *Petroleum, 9*(3), 317–330 https://doi.org/10.1016/j.petlm.2022.01.006

Said, M., Haq, B., Al Shehri, D., Rahman, M. M., Muhammed, N. S., & Mahmoud, M. (2021). Modification of xanthan gum for a high-temperature and high-salinity reservoir. *Polymers, 13*(23), 4212. https://doi.org/10.3390/polym13234212

Sanyal, S., Bhui, U. K., Kumar, S. S., & Balaga, D. (2017). Designing injection water for enhancing oil recovery from kaolinite laden hydrocarbon reservoirs: a spectroscopic approach for understanding molecular level interaction during saline water flooding. *Energy and Fuels, 31*(11), 11627–11639. https://doi.org/10.1021/acs.energyfuels.7b01648

Saputra, I. W. R., Adebisi, O., Ladan, E. B., Bagareddy, A., Sarmah, A., & Schechter, D. S. (2021). The influence of oil composition, rock mineralogy, ageing time, and brine pre-soak on shale wettability. *ACS Omega, 7*(1), 85–100. https://doi.org/10.1021/acsomega.1c03940

Sarkar, D., Sen, D., Nayak, B., Bhatt, P., Deo, M., & Dutta, B. (2018). Biopolymer assisted synthesis of silica-carbon composite by spray drying. *Colloids and Surfaces B: Biointerfaces, 165*, 182–190. https://doi.org/10.1016/j.colsurfb.2018.02.040

Seyyedi, M., Sohrabi, M., & Farzaneh, A. (2015). Investigation of rock wettability alteration by carbonated water through contact angle measurements. *Energy & Fuels, 29*(9), 5544–5553. https://doi.org/10.1021/acs.energyfuels.5b01069

Singh, K., Bijeljic, B., & Blunt, M. J. (2016). Imaging of oil layers, curvature and contact angle in a mixed-wet and a water-wet carbonate rock. *Water Resources Research, 52*(3), 1716–1728. https://doi.org/10.1002/2015WR018072