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A critical review of carbonate reservoir wettability modification during low salinity waterflooding

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ABSTRACT

The nature of carbonate reservoirs promotes the adsorption of oil onto the rock surface hence making oil recovery a challenge even with the interventions of varied chemical EOR methods. Recently, low salinity water flooding has become of great interest since it is cost-effective and environmentally friendly. Although low salinity waterflooding has been highly investigated in sandstone reservoirs, it is not the same for carbonate reservoirs due to its complexities. Nonetheless, it has been proposed as a favourable technique to mobilise the trapped oil in carbonate reservoirs. Wettability alteration is regarded as the most accepted mechanism for low salinity flooding but has not been well understood making field scale applications doubtful. In this paper, we present a detailed review of the wettability alteration mechanisms in carbonate reservoirs during low salinity waterflooding. Parameters influencing wettability alteration in carbonates and the interactions that occur at the rock/brine/oil interface are also presented. The different methods utilised for wettability measurements during low salinity waterflooding are also reviewed including their drawbacks and advantages and recommendations. This will provide an improved understanding of the low salinity flooding application in carbonate reservoirs.

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1. Introduction

Boosting crude oil production from petroleum reservoirs is an essential practice to increase oil revenue and promote sustainability [1]. Over the years, studies have shown that over 50% of the global oil reserves remain confined and unrecovered in carbonate reservoirs. After the initial stages of oil production, a reasonable volume of residual oil is left trapped in the reservoir. To date, enhanced oil recovery (EOR) methods are utilised in carbonate reservoirs to produce the remaining oil and increase recovery. EOR comprises of fluid/fluids injection into the petroleum reservoir to boost oil production after secondary pressure maintenance by injecting gas/water. The injected fluids can result in the change of the existing rock/oil/brine interactions in the reservoir thus promoting the recovery of the trapped residual oil. These interactions can be swelling of the oil, rock wettability modification and oil/water interfacial tension reduction [2,3]. It is well accepted that EOR projects are strongly affected by the economics and price of crude oil. Hence, the commencement of an EOR project relies on the preparation and willingness of investors to manage both the risk and economic investments [4]. Increasing oil production through EOR methods is a very crucial subject in the oil industry. Especially as carbonate reservoirs possess a very essential role in the future of the petroleum industry. Although increasing oil production from carbonate reservoirs may be one of the solutions to the world's energy demand. It is also vital that new techniques are developed and adopted to extract a substantial amount of oil for the sustainability and profitability of the oil and gas industry [5,6].

Carbonate reservoirs comprise of fractures of different sizes and lengths which can vary from very small to kilometres wide fissures [7–11]. The main mechanism that controls production in carbonate reservoirs is the communication between the fractures and rock matrix via capillary and gravity forces [12]. When EOR techniques

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are employed, the injected fluids are most likely to seep through the fractures and evade the oil in the porous media. The high permeability in the fractures with a corresponding low pore volume frequently results in the early production of the injected fluids. Furthermore, oil recovery from carbonate rocks is a challenge due to the nature of the neutral to oil-wet wettability [13–15]. Meaning that the oil will adhere to the walls of the carbonate rock making flow out of the reservoir difficult hence resulting in lower hydrocarbon recovery rates [4,16]. Rock wettability influences the location, distribution, and flow behaviour of the fluids in the reservoir. This in turn affects the relative permeability, electrical properties, capillary pressure and enhanced oil recovery performance [17–19]. The calcite present in carbonate rocks has been reported to possess a positive surface charge and when the carboxylic acid present in crude oil is adsorbed on the positively charged surface it creates an oil-wet state on the surface of the rock. The presence of asphaltene in crude oil also has a great effect on crude oil/brine the interfacial mechanism. Asphaltene binding occurs at the interface hence affecting the interfacial tension [20,21]. This contributes to the high residual oil in carbonate reservoirs which can be about 50%–68%.

In this paper, we aim to provide a detailed review of carbonate rock wettability alteration during low salinity waterflooding, and the underlying mechanisms. Also included is an in-depth review of the different methods that have been applied to measure changes in wettability during low salinity waterflooding. This will include standard and novel methods. This paper will also highlight the challenges/limitations and benefits of each technique by providing a thorough evaluation of these proposed methods based on their applications in the literature. To our knowledge, publications on wettability alteration in carbonates have only focused on chemical wettability modifiers such as surfactants and nanoparticles. Only very few have discussed wettability change in carbonate reservoirs during low salinity waterflooding.

This paper organisation is as follows: section 1 of this paper will introduce the topic. Low salinity waterflooding as a potential EOR technique will be introduced in section 2. The underlying mechanisms of wettability alteration and parameters affecting wettability alteration in carbonate reservoirs will be discussed and a summary of this section is included. This is followed by section 3 in which the methods of wettability measurement will be reviewed, and the benefits, limitations of these methods will be highlighted. In section 4, the concluding remarks from this comprehensive review will be discussed.

Reservoir rock wettability is identified as the ability of a fluid to spread or adhere to the surface of the rock when other fluids are present. it is also defined as the measure of affinity the rock has to either the water or oil [22–24]. The wettability of the reservoir is mostly dependent on the oil/brine/rock interactions. It is commonly accepted knowledge that the petroleum reservoir was initially occupied by water which was then followed by the migration of oil afterwards. As the oil migrates into the reservoir, it displaces the water but not entirely because of the water-wet nature of the rock minerals. Thus, initiating a thin water layer that coats the rock's surface. This thin layer works as an obstruction between the oil and the surface of the rock. If the thin water layer is sustained throughout the reservoir life, the water-wet condition of the reservoir will be conserved. The reservoir wettability can only be altered when this thin water layer is destabilised due to the oil/water/rock interactions. The destabilisation takes place when the force of attraction between brine/rock and oil/brine interfaces is greater than the repulsion forces. Causing it to collapse and allowing the oil to contact the rock surface. The heavy fractions present in crude oil contain components that adhere to the surface of the rock and create a wettability change from water to oil-wet [25–27].

Wettability modification from oil to water-wet by chemical treatment has been known to be one of the key techniques involved in releasing oil trapped in carbonate reservoirs [15,28,29]. Chemicals such as surfactants, alkali have been applied in the oil field and laboratory experiments to increase oil production by changing the wettability of rock. Austad et al. [30] demonstrated in their work that injecting surfactant into chalk can alter its wettability from oil to water-wet with a resultant increase in oil recovery. Seethepalli et al. [31] examined the interactions of dilute alkaline surfactant solution on carbonate mineral surfaces. They reported that the anionic surfactant modified the rock wettability from oil to intermediate/water-wet and worked better compared to the cationic surfactant. Hosseini et al. [32] studied the influence of alkaline/surfactant dilution on the wettability of carbonate rocks, oil recovery and relative permeability. They reported from their results that cationic surfactants had the greatest impact on wettability change and interfacial tension reduction in carbonates when compared to anionic and non-ionic surfactants. Standnes and Austad [33] examined the wettability alteration of carbonates by using non-hazardous and low-priced amines as cationic surfactants. They explained that wettability alteration is due to the release of the deeply adsorbed carboxylate groups from the rock surface by ionic pair creation.

Recently, the use of nanoparticles for wettability alteration has gained a lot of interest. Nwidee et al. [34] researched the impact of nickel (II) oxide (NiO) and zirconium (IV) oxide (Z_rO_2) on fractured limestone wettability. They conveyed that ZrO_2 has a better proficiency in shifting the oil-wet nature of limestone strongly water-wet. Moghaddam et al. [35] studied the influence of several nanoparticles on the wettability of carbonate rocks. They proposed that the structural disjoining pressure gradient generated a shift in wettability from oil to water-wet. The major limitation of these chemical wettability modifiers is the cost. Synthetic surfactants are very expensive. Thus, making the process of surfactant EOR non-economical. Furthermore, the environmental impact of surfactants is of great concern [36]. Additionally, the synthesis of nanoparticles for EOR incurs a huge cost to determine the optimal concentration required to alter rock wettability. This is of utmost importance because a highly concentrated nanoparticle injection fluid can lead to the blockage of the reservoir pores [37]. Due to the challenges encountered with the use of chemicals to modify rock wettability, many researchers have investigated novel techniques for improving oil recovery at a low cost and with a lesser impact on the environment. A good example of this technique is low salinity waterflooding (LSWF).

2. Low salinity waterflooding (LSWF)

LSWF technique involves the modification, diluting and tuning of the injection water ionic concentration to improve oil recovery [38]. Compared to other chemical EOR methods, LSWF offers a low cost and environmentally friendly means of increasing oil recovery. Due to the availability of water, low operational cost and less formation damage with the exemption of expensive chemical injection [39,40]. Martin [41] first discovered low salinity waterflooding by injecting freshwater to displace viscous fluids and increase oil recovery. Tang and Morrow [42] developed the original ideas of changing brine composition for improved oil recovery. Since then, extensive studies have been conducted by Refs. [23,42–54] on LSWF in sandstones and carbonates. Although an increase in oil recovery has been recorded in various studies, only a few pilot tests in carbonate reservoirs have been conducted [55,56]. This is because the underlying physiochemical interactions have not been fully understood [57].

Various mechanisms have been suggested for LSWF in carbonate reservoirs, and to date, there has not been a consensus on the underlying mechanisms. Due to the complex chemical interactions between the carbonate rock/brine and oil system. Also, the complexities of carbonate reservoirs have made upscaling the laboratory experiments to field scale application difficult and doubtful [58]. The commonly accepted mechanism for LSWF in carbonate reservoirs is the alteration of the rock wettability from oil to water-wet [59,60]. Although there have been reports that low salinity brine altered carbonate rock wettability from oil to water-wet, few studies have presented wettability alteration to an intermediate wetting state [61,62]. To fully grasp this wettability alteration in carbonates during LSWF, it is imperative to understand the underlying chemistry that promotes this mechanism.

2.1. Mechanisms for wettability alteration in carbonates during LSWF

The suggested mechanisms to describe rock surface wettability alteration in carbonate reservoirs include multicomponent ion exchange (MIE), electric double layer expansion (EDL) and mineral dissolution. These have been proposed to generate the main interactions that occur when carbonate rocks are subjected to LSWF. This, in turn, leads to the solid-liquid interaction behind wettability alteration [63].

2.1.1. Multicomponent ion exchange (MIE)

MIE was proposed by Austad et al. [64] as the main drive for wettability change in carbonates for LSWF. Fathi et al. [65] and Moradpour et al. [66] recommended that for MIE to occur, the potential determining ions (PDI) (Ca^{2+}, Mg^{2+} and SO_4^{2-}) must be present in the injection brine. MIE entails the adsorption of the negative charged sulphate ions onto the positively charged carbonate surface usually at the typical reservoir pH (6.4–7.5). Thus, reducing carbonates surface positive charge. This leads to the potential determining cations (PDCs) (calcium and/or magnesium ions) to adhere to the rock surface due to the lower electrostatic repulsion. At the oil-wet surface of the rock, calcium and magnesium react with the adsorbed surface-active components from the oleic phase, releasing some of them and in turn diminishing the oil-wet nature of the rock surface [67]. According to Ding [68] and Strand et al. [69] MIE is temperature-dependent and involves the following interactions:

(1) The $-COO^-$ fractions in crude oil interacts strongly with the Ca^{2+} ions in the calcite lattice through ligand bridging interactions. Hence, making the surface of the calcite oil-wet.
(2) At low temperatures between 20°C and 70°C, the adsorption of SO_4^{2-} ions makes the carbonate rock surface to be more negative. This decreases the electrical repulsions between the rock surface and aqueous Ca^{2+} ions. Thus, making the Ca^{2+} ions more attracted to the surface to interact with the $-COO^-$ fractions. Therefore, releasing the oil molecules from the calcite surface because the cation bridging interactions (>Ca-OOC) are much weaker than the ligand bridging interactions. On the contrary, the Mg^{2+} ions prefer to form ion pairs with SO_4^{2-} ions in the aqueous solution at low temperatures and due to their low activity, the Mg^{2+} ions will not react with the oil molecules at low temperatures.
(3) Lastly, at high temperatures between 100°C and 130°C, the Mg^{2+} ions happen to be more active causing the substitution of Ca^{2+} on the calcite surface. This substitution will cause the Mg^{2+} ions to react with $-COO^-$ fractions in the oil and then cause the oil to be released from the carbonate surface.

Egbe et al. [39] created a geochemical model to investigate the application of LSWF in carbonates. They proved that multicomponent ion exchange is responsible for wettability alteration. Srisuriyachai and Meekangwal [70] conducted core flooding experiments to provide evidence of MIE in dolomite formation during LSWF. They attributed the oil recovery increase to wettability alteration caused by MIE. Moradpour et al. [66] with the aid of numerical modelling and core flooding experiments indicated that MIE is the reason for a shift in calcite wettability to water-wet from oil-wet. They postulated that MIE is a time dependent reaction, and a soaking time of 48 h is required for the potential determining ions to achieve the highest level of substitution. Adegbite et al. [71] performed geochemical modelling and included the MIE mechanism to study LSWF effect on oil recovery. They concluded that wettability change is the reason for increased oil recovery. Bazhanova and Pourafshary [72] performed a spontaneous imbibition test to examine wettability change in carbonates. They agreed that the adjustment of salinity and active ions can trigger MIE mechanism. Also, a salinity level of 15,000 ppm can initiate MIE to alter the wettability of carbonates. Fig. 1 illustrates multicomponent ion exchange in carbonates.

2.1.2. Mineral dissolution

Hiorth et al. [21] and Al-Shalabi et al. [74] suggested calcite dissolution as the prime mechanism for wettability modification in carbonates during LSWF injection. They stated that before LSWF in carbonate reservoirs, all the reactions in the reservoir achieve an equilibrium state. When the LSWF injection brine contains more SO_4^{2-} ions than formation water in the reservoir, the earlier equilibrium between the carbonate rock, formation water and crude oil is disturbed. Leading to an increase in the precipitation of anhydrite ($CaSO_4$). This causes the loss of Ca^{2+} concentration in the aqueous phase. To offset the loss of Ca^{2+} ions, the dissolution of calcite minerals increases. If the dissolution of calcite happens at the areas where the oil molecules adsorb, the oil molecules will be liberated from the rock surface. Exposing the initial water-wet condition of the carbonate surface. Proving that the oil-wet carbonate surface has been altered to water-wet due to the oil detachment by calcite dissolution [68]. Fig. 2 demonstrates the calcite dissolution mechanism during LSWF.

Al-Shalabi and Pope [74] with the aid of the geochemical simulator PHREEQC, modelled the recovery mechanism behind LSWF in carbonates by matching published experimental results with their model. In their findings, the surface charge/rock surface dissolution caused wettability alteration. Yousef et al. [56,75] using NMR experiments demonstrated that calcite dissolution could lead to the enlargement of the pore sizes as well as enhance the connectivity between the micro and macropores. They suggested that wettability alteration due to calcite dissolution can lead to an increase in oil recovery. Pu et al. [76] executed core flooding experiments to study the oil recovery potential of LSWF. They concluded that in addition to mineral dissolution, other mechanisms, such as the solubilisation of rock components with lower solubilities than anhydrite, the removal of the outermost molecular layer of the pore lining material and the release of adsorbed organic materials are responsible for wettability alteration. On the contrary, Nasralla et al. [77] proposed an experimental approach to understanding the mechanisms of LSWF. They implied that rock dissolution is not responsible for wettability alteration during LSWF in carbonates. They observed a wettability change to a less oil-wet state in their experiment without rock dissolution. Mahani et al. [78] combined experimental and theoretical modelling methods to study LSWF in carbonates, they disagreed that calcite dissolution is responsible for wettability alteration. They observed a shift in wettability of calcite to water-wet without dissolution. They further discussed that rock dissolution is only relevant in the laboratory and not reservoir scale.

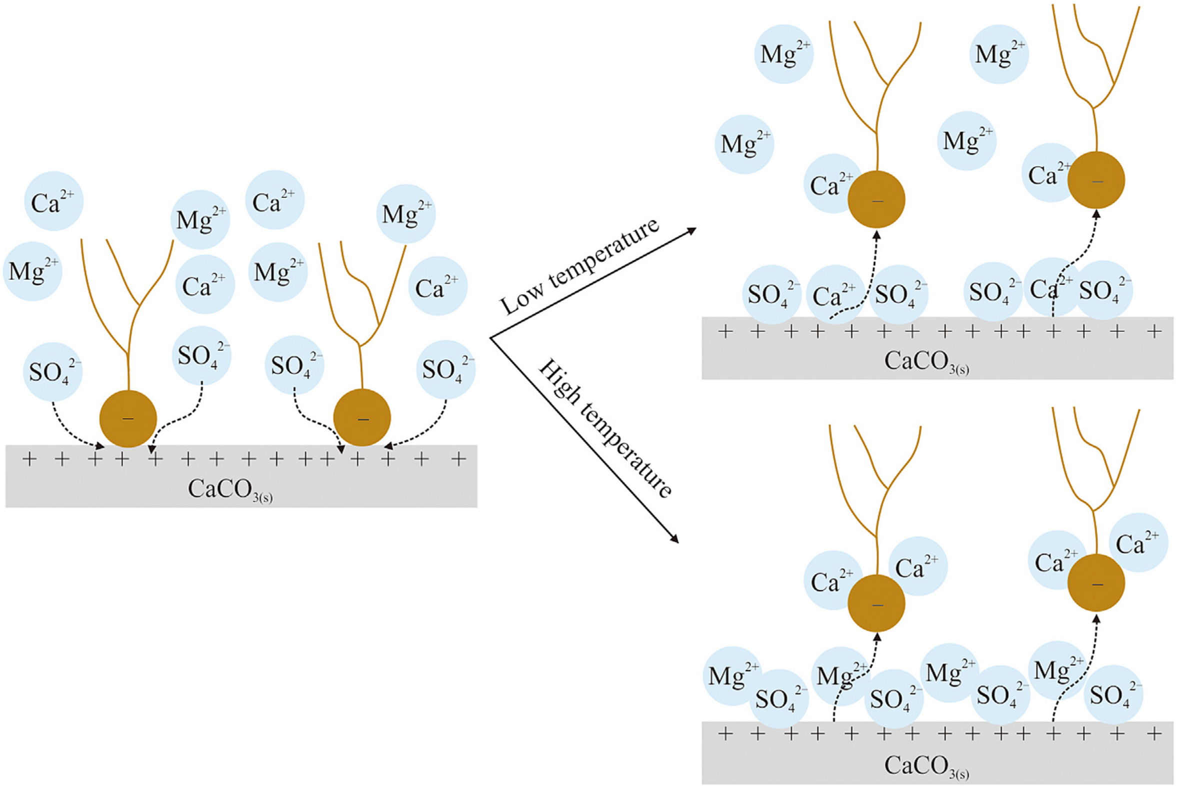

Fig. 1. Multicomponent ion exchange in carbonates [73].

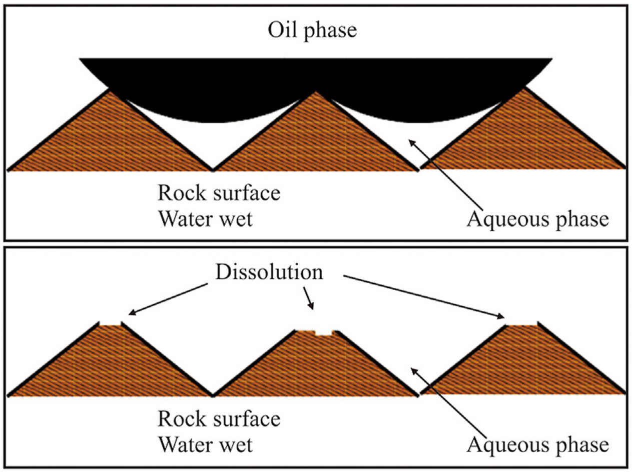

Fig. 2. Calcite dissolution mechanism [21].

2.1.3. Electric double layer (EDL) expansion

According to Ahmadi et al. [53] wettability alteration of carbonates is directly linked to the influence of the variation in the electric double layer. EDL describes ion distribution in the aqueous region of the reservoir rock [79]. An electrically charged surface such as calcite once in contact with an aqueous solution generates an electrical field which results in an unequal distribution of ions in the surrounding area at the surface. The oppositely charged ions in the aqueous solution (counter-ions) are drawn to the surface to create a charged diffuse layer outside the charged surface. While the ions with a similar charge to the surface (co-ions) will be deterred from the surface. This diffuse layer and the surface charge together form the electrical double layer. The counter-ions within the double layer are not equally distributed, hence a potential across the interface is developed. Some of the counter-ions are strongly adsorbed onto the surface creating a fixed layer known as the Stern layer. The stern layer which is adjacent to the mineral surface is further divided into the inner and outer Stern layer or planes. The chemistry of the injection brine has been identified as a major factor influencing the thickness of the electric double layer. Therefore, in low salinity studies, the electric potential of the surface at the location of the shear or slip plane is used to characterise or demonstrate wettability alteration [80,81]. The EDL mechanism in carbonate rocks is presented in Fig. 3.

Experimental studies conducted by Alotaibi et al. [83] on LWSF showed that the highly negative charge on dolomite and limestone particles was created by the expansion of the EDL thickness. Heberling et al. [84] used a stern surface complexation model to examine the zeta potential of calcite in LSWF brine. They suggested that the fundamental mechanism for wettability alteration in calcite can be attributed to the dynamics of the electric double layer formed at the interface down to a few nanometers. Fathi et al. [85] in their study of ion composition and salinity on the wettability alteration of chalks, performed spontaneous imbibition and chromatographic wettability experiments. They discussed that the double layer effect is necessary for wettability alteration to take place. Myint and Firoozabadi [86] in their review of wettability alteration in carbonates, stated that the double-layer expansion is closely related to the thickness and stability of the brine films. Sari et al. [87] in their study combined surface complexation modelling, contact angle and zeta potential measurements to examine the potential of LSWF. They confirmed that the electric double layer is responsible for wettability alteration in carbonates. They proposed that the electrostatic charges between oil/brine and brine/calcite interfaces became more negative with a decrease in the brine salinity. On the contrary, Kazankapov [88] conducted spontaneous

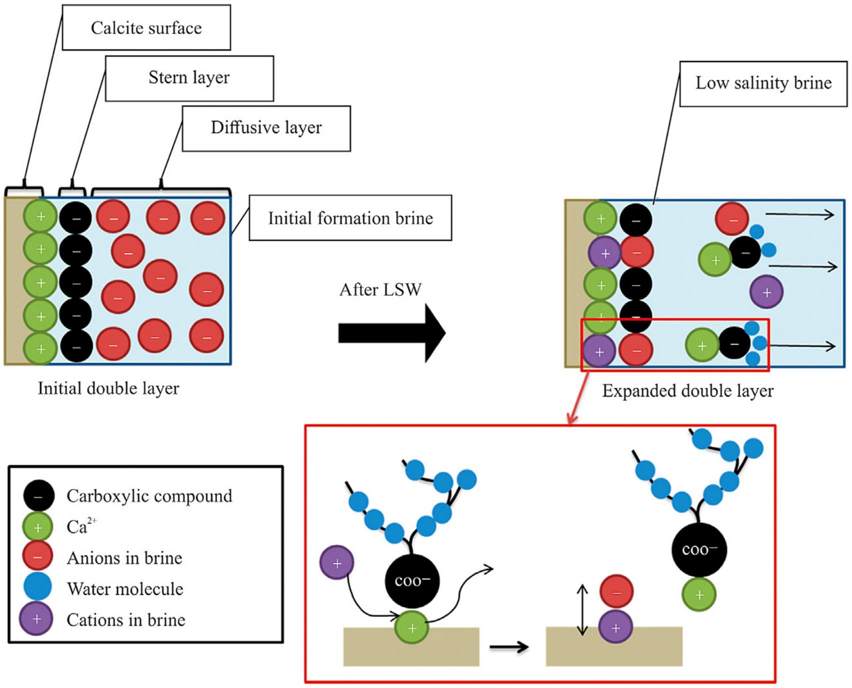

Fig. 3. Electric double layer mechanism [82].

imbibition and chromatography wettability experiments to study LSWF in carbonates. They discussed that the electric double layer was not a contributing factor to the wettability alteration of Caspina carbonates in their study.

2.2. Factors affecting wettability alteration in carbonate reservoirs

Several factors such as pH, salinity/ionic strength, oil composition, temperature and rock mineralogy have been proposed to affect wettability alteration of carbonates in LSWF [1].

2.2.1. pH

The formation water of carbonate reservoirs is slightly basic between 7 and 9. Experimental results have demonstrated that the injection of diluted seawater can increase the pH due to calcite dissolution. Yet, according to Derkani et al. [1] and Austad et al. [64], the pH of carbonate reservoirs remains unaffected due to the high buffer capacity from the formation water and the chemical equilibrium at the brine/oil/rock interface. They considered pH variation as a temporary mechanism for wettability alteration.

Zhang et al. [89] from their chromatographic wettability test speculated that there is a certain pH level that can trigger a strong water-wet state due to the H^+ ion adsorption at the interface. Gomari and Hamouda [90] carried on contact angle measurements to examine the effect of LSWF on calcite. They agreed that the extent of calcite wettability change is dependent on the pH. Xie et al. [91] performed geochemical modelling and contact angle measurements to examine the pH effect on oil/rock/brine interactions. They demonstrated that pH is one of the dominating factors in wettability alteration in carbonates during low salinity waterflooding. In their conclusions, they stated that at a low $pH < 5$ an adsorption of H^+ ions at the carbonate/brine and oil/brine interface can be initiated. Chen et al. [92] studied LSWF in carbonates using contact angle tests and surface complexation modelling. They observed that at certain pH levels, oil-wet conditions can be triggered in carbonate systems during LSWF. This explains why the LSWF effect is not detected in some carbonate reservoirs. Sari et al. [87] examined the impact of pH on the wettability of carbonate reservoirs. They suggested that a low pH of 3 has more impact on calcite wettability than ion modification, reduction in salinity and increase in temperature. Saikia et al. [93] in their experimental studies, explored wettability alteration in carbonates during LSWF. They proposed that the further away the pH of the brine is from the isoelectric point of the carbonate, the higher the chances of wettability alteration. Chen et al. [94] examined the effect of salinity and pH on wettability by performing geochemical modelling. They reported that the pH increase of the brine has more effect on wettability alteration of calcite than the presence of calcium ions.

2.2.2. Salinity/ionic strength

Studies have shown that these two different approaches are responsible for wettability alteration in carbonates during LWSF [95].

1. Successive dilution of formation brine/seawater and their injection into the reservoir in secondary and tertiary mode. Thus changing the salinity and ionic strength of injection brine.
2. Tuning of the ionic composition of seawater by keeping the ionic strength constant and altering the concentrations of the PDIs.

Karimi et al. [96] investigated wettability modification and oil recovery in carbonates by conducting spontaneous imbibition experiments. They reported that the presence of magnesium and sulphate ions in the injection brine altered calcite wettability from oil to water-wet. Furthermore, they stated that a modified brine with higher sulphate ions has more efficiency in altering wettability compared to magnesium ions. Gandomkar and Rahimpour [97] assessed the impact of divalent and monovalent ions on limestone wettability using contact angle measurements. They reported that the limestone surface has a very strong affinity to SO_4^{2-}, Mg^{2+} and Ca^{2+}. Vajihi et al. [98] used capillary pressure measurements to investigate the influence of LSWF on limestone cores wettability. Their results showed a shift in the wettability index to a more water-wet state. The effect of individual ions on wettability alteration in carbonate rocks was examined by Rashid et al. [99]. They applied the contact angle and spontaneous imbibition tests for their study. They verified that Mg^{2+} alone can alter the wettability of carbonate rock and SO_4^{2-} works as a catalyst for Mg^{2+} and Ca^{2+}. Høgnesen et al. [100] from their experimental studies concluded that modifying the injection water ions can influence carbonate rock wettability resulting in additional oil to be recovered. Shariatpanahi et al. [101] conducted a chromatographic surface reactivity test. They concluded that the presence of Mg^{2+} in the formation water increases the water-wetness of calcite surface compared to Ca^{2+} and the dolomite surface has a lower affinity to polar carboxylic materials compared to calcite. Alshaikh and Mahadevan [102] performed a sensitivity study on the impact of brine composition on calcite wettability. They discussed that for the wettability of calcite to change from oil to water-wet, a moderate reduction in salinity is necessary with a decrease in divalent ion concentration and an increase in sulphate ion concentration. Gupta and Mohanty [29] used contact angle measurements to examine wettability alteration of fractured carbonate rocks. They reported that by reducing water salinity, calcite wettability can be modified to a more water-wet state and sulphate ions are only active when magnesium and calcium ions are present. Shaik et al. [103] performed contact angle measurements to study the effect of salinity and ionic strength on wettability of calcite rocks. They proposed that with a brine ionic strength of 0.164 M the wettability of calcite surface can shift from oil to water-wet regardless of the brine composition.

It has been noted in the literature that apart from Ca^{2+}, Mg^{2+} and SO_4^{2-} as PDI, other ions such as Phosphate (PO_4^{3-}) and Borate (BO_3^{3-}) can trigger wettability change in carbonates. Meng et al. [174] used the contact angle measurements to observe the effect of PO_4^{3-} ions in the wettability alteration of carbonates. The results from their measurements showed that a high concentration of PO_4^{3-} in low salinity brine can alter wettability to a less oil state at a rapid rate. They also observed that at low concentrations of PO_4^{3-}, the wettability alteration was weak. Gupta et al. conducted core flooding experiments and numerical simulations on low salinity waterflooding. They used different low salinity brines spiked with PO_4^{3-} and BO_3^{3-} and SO_4^{2-}ions. They reported that the increase in oil recovery was due to the wettability change and brines spiked with PO_4^{3-} and BO_3^{3-} performed better than SO_4^{2-} brine.

2.2.3. Oil composition

Crude oil composition is regarded as one of the key parameters that can affect wettability alteration during LSWF. The presence of polar components in oil is necessary for LSWF to create wettability alteration [104]. The interaction of the polar components dominates in the absence of a water film that exists between the oil/rock. While the surface-active elements of crude oil are found in an ample range of petroleum fractions, they are more common in heavier fractions such as resins and asphaltenes. These are believed to be polar components that contain oxygen, nitrogen, and sulphur with a very strong interfacial activity that can alter the wettability of a mineral surface. One end of the molecules contains sulphur, oxygen and nitrogen. These are known as organic acid and base compounds which can easily be adsorbed on the mineral surface by Coulomb force or hydrogen bond. The other end is the alkyl group which is exposed outside and leads to the enhancement of oil affinity on the rock surface [105,106]. The acid and base components of crude are identified by the total acid number (TAN) and total base number (TBN) of crude oil [107,108].

To further understand the effect of oil composition on wettability alteration in carbonates, Takeya et al. [109] used a combination of zeta potential measurements and surface complexation modelling to investigate the impact of oil acid number on the carbonate electrokinetic properties. They discussed that in LSWF, the water wetness of carbonate rocks declines with an increase in acid number. This was credited to the strong bond generated between the crude oil negative charge and the carbonate positive surface. Al-Balushi et al. [108] employed several analytical methods (interfacial tension, zeta potential and contact angle measurements, Fourier transformed infra-red and fluorescent ultra-violet spectroscopy) to study the effect of acid and the base numbers of a model oil on wettability alteration of calcite surfaces. They reported that high concentrations of acid components shift calcite wettability to a more oil-wet state while increasing the base number modified the wettability to an intermediate-wet state. Mwangi et al. [110] with the aid of the modified floatation technique conducted wettability measurements to investigate the effect of organic acids on wettability change in carbonates. They discussed that long-chained organic acids increased the oil wetting state of carbonate with diluted seawater while short-chained organic acid had the opposite effect.

2.2.4. Rock mineralogy

Most carbonate reservoirs contain minerals other than calcite such as quartz, anhydrite and dolomite. These minerals can affect the rock/brine/oil interactions that lead to wettability alteration and improved oil recovery. Qiao et al. [52] developed a mechanistic model for wettability to understand the role of rock mineralogy in low salinity waterflooding. Their studies involved the application of LSWF in Clint chalk samples composed of 100% calcite and limestone cores composed of calcite and anhydrite. They explained that dilution of seawater can alter the wettability of limestone due to the presence of anhydrite but for chalks, the wettability can only be altered by the injection of specific ions. Romanuka et al. [111] investigated the role of carbonate mineralogy on LSWF using three different types of carbonate rocks (chalk, dolomite and limestone). They performed the Amott spontaneous imbibition experiment in their study. They reported that chalk samples did not respond to seawater dilution but tuning of the sulphate concentration led to a change in the wettability. Furthermore, for the limestone and dolomite samples, anhydrite dissolution occurred due to dilution which resulted in wettability change. Their results were in agreement with that of Qiao et al. [52]. Su et al. [112] presented in their core flooding study that the higher the calcite content in the rock the greater the wettability change during LSWF. Fernø et al. [113] used spontaneous imbibition experiments to investigate the effect of rock mineralogy on wettability. They suggested that depending on the mineral depositions and variations in the rock composition, the outcrop rocks exhibit diverse reactivity to SO_4^{2-} ions. They further stated that limestone outcrop responded differently to SO_4^{2-} ions when compared to reservoir limestone.

2.2.5. Temperature

According to Al-hadhrami and Blunt [2], wettability alteration in carbonate reservoirs is temperature dependent due to its effect on the mineral/water and oil/water interfaces. Hamouda and Gomari [114] applied zeta potential and contact angle measurements to examine the effect of temperature on calcite wettability during LSWF. They concluded that at elevated temperature, the wettability of the calcite was modified to water-wet from oil-wet. By combining experimental and theoretical approaches, Mahani et al. [115] executed their study on the temperature effect on LSWF. They agreed that increasing temperature can increase the change in contact angle to a less oil-wet state, but it depends on the type of the rock. Tweheyo et al. [116] employed the chromatographic wettability and contact angle tests in their study of temperature effect on wettability alteration in carbonates. They discussed that wettability alteration in carbonates during LSWF is temperature dependent. An increase in temperature from 70°C to 100°C will activate the adsorption of sulphate on the calcite surface. Hence shifting the wettability to water-wet. Zhang et al. [117] in their study, conducted core flooding experiments, zeta potential and spontaneous imbibition tests to examine temperature effect on ion exchange mechanism in LSWF. They discussed that at low temperatures, there is no substitution reaction between Mg^{2+} and Ca^{2+}. While at high temperatures between 100°C and 130°C, Mg^{2+} substitutes Ca^{2+} at the chalk surface. This interaction will release Ca^{2+} and interact with the crude oil releasing it from the surface. Zhang and Sarma [118] used core flooding experiments in their study of LSWF in carbonates. They observed an enhancement of water wetness in carbonate rocks at 90°C by reducing salinity or increasing sulphate concentration. Zhang and Austad [13] in their experimental study of LSWF indicated that the adsorption of SO_4^{2-} increased drastically as the temperature was increased beyond 100 °C and increasing temperature with calcium/sulphate ratio can promote the water wetness in chalks.

2.3. Summary

Regarding the three mechanisms of wettability alteration in carbonates for low salinity waterflooding, Ca^{2+}, SO_4^{2-} and Mg^{2+} can work together or separately. These ions which are also known as the potential determining ions play essential roles in wettability alteration. Although the presence of SO_4^{2-} is very crucial, a high concentration of SO_4^{2-} can lead to scaling and souring in the reservoir. Ions such as PO_4^{3-} and BO_3^{3-} have shown to be good candidates for wettability change and can be great replacements for SO_4^{2-} but more studies are required to understand the interactions with these ions [119,120]. According to Mahani et al. [78] mineral dissolution does not contribute to wettability alteration for field applications because, at reservoir scale, the brine will equilibrate with the minerals from the rock as the displacement front advances. Furthermore, mineral dissolution is a secondary and not a primary mechanism for wettability alteration. Additionally, for the EDL mechanism to occur, the rock surface must be negatively charged for cation bridging to occur with the negatively charged polar oil compounds.

There have been contradicting results in terms of wettability alteration mechanisms. This is to say that although these mechanisms can occur, there are underlying factors that can trigger each or all these mechanisms during LSWF. The success of LSWF in altering the wettability of carbonates depends on the chemistry between influencing factors discussed in section 2. It is also important to characterise the rock, oil, and brine samples, as it has been shown from the literature that the rock (mineralogy), oil (Acid/Base number) and brine (salinity, ionic composition) properties are responsible for the contradicting results in LSWF in carbonates. An optimum LSWF injection brine is required to trigger wettability change. Some carbonate rocks will respond to ion modification rather than salinity reduction due to their mineralogy. Temperature also plays a critical role, as demonstrated in the literature. Increasing temperature activates and promotes interaction between ions leading to a more water-wet state.

Given the importance of wettability to understanding the concept of recoverable hydrocarbons from a reservoir, the accuracy of the measurement methods needs to be considered. The fact that most carbonate rocks are fractured and the production of hydrocarbons is attributed to these fractures than the matrix, causing significant limitations to the accuracy of wettability measurements on core samples [11]. A review of the methods used for wettability measurements in carbonate rocks, their advantages, limitations and comparisons of these methods is presented in the next section.

3. Wettability measurement methods used for LSWF in carbonates

Alotaibi et al. [121] emphasised the challenges of tracking the wettability change in carbonates rocks (calcites and dolomites) when they considered the optimum salinity that alters the oil-wet conditions of the rocks. They mentioned that there was confusion as to understanding the point at which the wettability changes from oil-wet to water-wet during low salinity water injection. Many other studies have encountered this same problem. Hence, the need fully understands the workings of these measurement techniques used in the literature.

Currently, according to Deng et al. [122], wettability measurements can be categorised into standard and novel methods. The standard measurements widely used in the industry are the contact angle measurement, Amott-Harvey, and the US Bureau of Mines (USBM) test.

3.1. Standard techniques

3.1.1. Contact angle

The most widely used technique is the contact angle measurement often referred to as the sessile drop method [123]. This method utilises a camera to capture the angle between the rock surface and the liquid (oil/brine). The surfaces to represent carbonate reservoirs are normally polished marble or calcite surfaces [90]. The contact angle is then determined using the camera to infer the tangent to the vapour-liquid interface. Based on the measured contact angles, a wettability criterion is used to determine the rock wettability relative to the fluid considered. A typical criterion is summarised in Table 1 as adapted from Ref. [124]. This shows the contact angle ranges for the different types of wettability states.

There are however varied factors that affect the contact angle measurement. These include temperature, droplet volume, oil acid number, salinity and surface smoothness [114]. This method works best with pure fluids and well-prepared surfaces limiting its application when used with reservoir rocks and oil. The limitation of the estimation of the contact angle method is that it excludes the pore structure nature of the sample but allows for only the single surface area wettability [125]. A dynamic contact angle wettability method also can be applied to improve on the measurements made by the static contact angle measurement. The typical procedure is to either add liquid to the droplet (base fluid) or reduce the droplet size on the surface considered. The addition process leads to the advancement of the liquid front on the surface while the reduction process leads to a withdrawal of the liquid front. The resulting contact angle measured under the addition process is termed the advancing contact angle while that of the reduction in droplet size is termed the receding contact angle. The lag in contact angles

Table 1
The ranges of contact angles to rock wettability type [124].

Wettability state	Contact angle
Water-wet	0–80
Mixed-wet	80–100
Oil-wet	100–180

relative to the addition and reduction process yields a hysteresis that can be used to ascertain rock surface roughness. Dynamic wettability measurements were performed by Sakthivel [126], to measure the wettability of a carbonate rock before and after low salinity flooding. Results of the receding and advancing contact angles were compared with core flooding performance to understand the dynamics of the low salinity concentration on oil recovery.

3.1.2. The Amott-Harvey method (AHM)

The Amott-Harvey test of macroscopic rock wettability as developed by Ref. [127] is performed based on two spontaneous and two forced imbibition processes. During the spontaneous imbibition processes, the fluid to be imbibed submerges the rock sample where the non-imbibed fluid is determined as the displaced volume. The forced imbibition processes are performed with core flooding or centrifuge equipment to flow the imbibing fluid through the rock sample with the intent to measure the volume of the displaced non-imbibed fluid. Fluid is displaced until it reaches residual saturation in the rock sample. For example, in the case of water and oil in carbonate rocks. Spontaneous imbibition is carried out in a water-filled tube with the core sample submerged, which is followed by forced imbibition of water via a core flood until oil residual saturation is reached. The oil is then re-imbibed into the carbonate core spontaneously via an oil-filled tube with a later forced imbibition process performed via a core flood. The Amott-Harvey test collects displaced and total volumes during the spontaneous and forced imbibition processes to estimate the Amott-Harvey wettability index I_{AH} as:

$$I_{AH} = \left(\frac{S_{wi}}{S_{wt}}\right) - \left(\frac{S_{oi}}{S_{ot}}\right) \tag{1}$$

where S_{wi} and S_{wt} are the imbibition water saturation and total water saturation respectively and S_{oi} and S_{ot} are derived from the displacement and total volumes of the imbibition process. Table 2 presents the rock wettability criteria for the values of the I_{AH} as adapted from Ref. [128]. It is noteworthy that most of the experiments can be conducted under high temperatures but not high pressures.

3.1.3. USBM method

The USBM method as developed by Ref. [129] considers a similar procedure as the Amott- Harvey test. It also considers the work done required to apply the forced displacement processes of the imbibed and non-imbibed fluids. The work done during the force process is determined as the area under the derived capillary pressure curve of the oil drive curve, A_o and water drive curves A_w [130]. The wettability in form of the USB index of the sample is then determined by the logarithm of the areas as such that:

$$I_{USM} = \log\left(\frac{A_o}{A_w}\right) \tag{2}$$

Similarly, a criterion to infer the average rock wettability based on the derived index is summarised in Table 3.

Time measurements given the complexity of wettability alteration in carbonates rocks needs attention. The novel methods tend to address this situation to an extent. The novel techniques though mainly qualitative inferences of wettability provide vital information on the dynamics of wettability changes.

Table 2
Wettability criteria for the Amott-Harvey test.

Wettability state	Amott-Harvey Index
Water-wet	0.3–1
Mixed-wet	-0.3–0.3
Oil-wet	-1–-0.3

3.2. Novel methods

The novel methods involve the use of pore scale scanning technologies or physical inference methodologies. These are employed to enhance the accuracy of wettability alteration measurements. These methods include Nuclear Magnetic Resonance (NMR), floatation test, Micro CT, Scanning Electron Microscope (SEM), Infrared spectroscopy and Thermogravimetric analysis (TGA) and Atomic force microscopy (AFM).

3.2.1. Nuclear Magnetic Resonance (NMR) method

The NMR method presents a faster and cheaper method for wettability measurement in rocks. This method is based on the detection of disparity in relaxation times in fluids that have a hydrogen atom. In the case of petroleum resources, oil and water define these fluids to be detected. The NMR has been applied to sandstone [131] and shale [132,133] samples with reasonable agreements with the Amott-Harvey method. Few investigations have however considered NMR with carbonate rocks given the extreme heterogeneity resulting from the complex pore structure and dual porosity in the case of fractured carbonate rocks. The NMR response is then converted into wettability indices where a criterion can be established. There have been quantitative interpretations by a notable number of researchers on carbonate rocks [134–136]. The accuracy is limited by the pore size of the rock samples. As cited in the review work of Ivanova et al. [123], the wettability W, from the NMR technique can be determined based on the logarithmic ratio of the relaxation times of the two fluids as such that:

$$W = log\left(\frac{T_{lm}^{oil}}{T_{lm}^{water}}\right) \tag{3}$$

where T_{lm}^{oil} and T_{lm}^{water} are the spectral times of the wetting and no wetting phases or fluids. Table 4 summarises the wettability criteria for the proposed analysis from the NMR method (see Table 5).

The NMR method can be used for brittle samples and the determination of the pore geometry, even though the accuracy of measurement is limited with a decrease in pore size. Hsu et al. [137] revealed that paramagnetic impurities in the carbonate rock (limestone) sample, affected the quality of the photon relaxation time, while the deuterium relation was affected by the surface wetting properties of the sample, though not affected by the impurities in the pore structure. It is hence clear that carbonate sample presents challenges in wettability measurements.

3.2.2. Micro CT (μ-CT) method

The micro-computed tomography of core plugs presents a visualisation technique of assessing residual phase distributions, contact angles and deduced wettability from captured tomography images of the targeted pore structure of the samples. Due to the recent improvements in micro-computed tomography (MCT) and

Table 3
Wettability criteria for the USBM method.

Wettability state	USBM Index
Water-wet	>0
Mixed-wet	~0
Oil-wet	<0

Table 4
Wettability criteria for the proposed NMR method.

Wettability type	NMR wettability
Water-wet	>0
Mixed-wet	~0
Oil-wet	<0

computing power, there has been a significant increase in pore-scale studies in recent years. Micro-CT imaging is a powerful non-destructive imaging technique that allows for a 3D visualisation of the interior of the rock including the intricate pore structures, fluid saturation and fluid/fluid interfaces within the porous media allowing for pore topology, fluid distribution and contact angles to be measured at reservoir conditions [138]. Few researchers have been able to develop the algorithms required to utilise this technology in measuring in-situ contact angles from the three-dimensional micro-CT [139,140]. Kumar et al. [141] recently applied the high-resolution micro-CT method to generate a three-dimensional tomography of a carbonate core plug, during a steady-state core flood experiment. Analysis of the images revealed the fast evolution of the contact angle corresponding to the wettability changes of strongly oil-wet from water-wet after contact with crude oil under the reservoir conditions. Tawfik et al. [67] examined carbonate wettability alteration during chemically tuned waterflooding (CTWF) in carbonate rocks. They advised that the use of micro-CT is necessary to fully understand the physiochemical interactions governing wettability alteration at the pore scale at different conditions in carbonates.

3.2.3. *Microscopic methods*

The microscopic method of wettability analysis presents a qualitative inference method where a video camera is used to capture images of the target core plug at the micro and nanoscales. These observations are normally made at laboratory temperature and pressure. Two main examples of microscopic methods include the Scanning Electron Microscope (SEM) and Atomic force microscopy (AFM) methods. Numerous versions of the SEM has seen recent applications by some researchers who considered core to pore-scale surfaces of carbonate rock samples to understand the wettability alteration mechanism under varied flooding conditions [142–144]. AFM method works based on force-distance measurement between a tip and a target surface. The image of the surface is then produced with repeated measurements that cover the surfaces [145]. Al Maskari et al. [146] utilised the AFM method to study the pH effect on brine/calcite and brine/oil interfaces. They confirmed that their result agreed with that measured using the contact angle method. AFM is used as an additional technique to detect wettability change, by studying the topographic and compositional surface changes of the rock [14]. The microscopic method however may be slower than other advanced methods with a high expense of the equipment needed.

Table 5
Comparison of the different wettability measurement methods.

Method	Advantages	Limitations
Static contact angle	Simple Fast method (1–2 h) Accurate Surface wettability	Impurities between droplet and surface can affect readings Heterogeneity of surfaces can affect readings Cannot provide information regarding organic coatings Cannot relate results directly to core flooding performances
Dynamic contact angle	Measures transient variations in contact angles Accurate in relating to core flooding performance Fast method (1–2 h) Applicable for high-pressure high-temperature conditions	Speed of increasing or decreasing droplet volume is critical
AHM	Reliable Core scale wettability investigation	Slow method (10 day) Expensive Non-effective under neutral wettability
USBM	Reliable Core scale wettability Sensitive to neutral wetting systems	Expensive Slow method (1–2 day) Requires multiple procedures to produce quantitative results Expensive
NMR	Very fast method (10 min) High pressure and Temperature conditions Studies wettability at the macro, micro scale and fractional wettability Noninvasive	Complex and expensive
Micro-CT method	In situ wettability Pore-scale investigation	Expensive Uses a radioactive source for measurement
Microscopic	In situ wettability alteration can be examined Sub pore-scale investigation Surface morphology investigation using (AFM and SEM)	Expensive Image resolution competing with processing power
Thermogravimetric Methods	Infers surface wettability from physically and chemically adsorbed matter.	May Require further validation studies Destructive technique Expensive
Infrared (IR) Spectroscopy	Relatively fast method Sub pore-scale investigation Characterises desorption from calcite	Expensive
Flotation Test	Very Fast method (1 h) Low cost	The effect of strongly wetted systems is critical
Zeta Potential	Sub pore scale investigations	Destructive methods as samples are crushed Requires carbonate and the solvent to be in equilibrium for accurate reading
SCM	Low cost, Fast and effective	Model prediction errors Isotherms developed for many ambient conditions Requires validation from other standard methods

3.2.4. Thermogravimetric method

In principle, thermogravimetric analysis (TGA) of a solid surface determines the mass disparity of an adsorbent relative to temperature variation [147]. This relation is made as a function of the strength of affinity of the adsorbent for the surface, hence the wetting properties of the sample can be inferred. Li et al. [148] in their study of wettability alteration due to varying concentrations of smart water in a carbonate sample, used the TGA to understand the adhesive nature of the fluid interaction with the rock sample. The results of their study were useful in understanding the recovery improvement brought about by the EOR method. Studies by Ahmadi et al. [149] and Pillai et al. [150] used TGA to investigate further the amount of brine that was absorbed by the carbonate sample under varying temperatures.

Since the samples are heated during the TGA, it is considered a destructive technique, hence limiting repeatability with the same core sample.

3.2.5. Infrared (IR) spectroscopy

Using Fourier Transform Infrared spectrums, the disparities in chemical bonding resonance frequencies can be employed to monitor wettability alterations in a core sample. The changes in peaks of the dominant wavenumbers in a spectrum of an emitted infrared spectrometer before and after an EOR procedure provides evidence of tuning the fluid composition effect in the target sample [29,151,152]. have all considered the use of IR spectroscopy on analysing wettability alteration in dolomite and chalk samples. Pillai et al. [150] investigated wettability alteration behaviour via detection of the presence and absence of functional groups within a dry carbonate sample rock and crude oil-aged carbonate sample via a Fourier Transform Infrared spectrophotometer in the 400 and 4000 cm^{-1} range. The dry sample showed absorption peaks that corresponded with stretching vibration of Ca—C bonds, indicating the presence of calcite. The peaks also were correlated with the crude oil functional group, such as the C—O bond (due to bending vibration) and O—H group which confirmed an oil-wet rock.

3.2.6. Floatation test

The flotation wettability measurement method provides a semi-quantitative indication of wettability alteration. The theory for the floatation test is that the oil-wet particles will float and while the water-wet particles sink. First, the rock sample is crushed and aged in the water and then the particles are separated and aged in oil for some time. Water is added to the rock-oil mixture and allowed to settle. The mixture is decanted afterwards, and the rock is weighed for the volume in either fluid. The ratio of the total volume is used to determine the wettability index. Some researchers have used the flotation test on carbonate rocks [110,153]. Thyne [154] developed a modified flotation technique to estimate wettability under reservoir conditions. The floatation test is less expensive and relatively faster than other methods in the novel category.

3.3. Other methods

3.3.1. Zeta potential measurements

Studies have established that the electrostatic forces between the brine/oil and brine/rock interfaces form the adhesive forces which dominantly control the wettability in carbonate rocks [155]. These forces can be measured based on the zeta potential that exists at the interfacial level of the fluid/solid and fluid/fluid interface. The zeta potential is defined as the average potential in the EDL at the shear zone which is between the mobile charged particle and the immobile liquid phase where a particle is suspended [156,157]. Zeta potential measurement is of specific importance because it detects the electrical properties of a charged rock surface [158]. The sign or charge of this parameter depicts the electrokinetic properties of a particle, while its magnitude explains the colloidal stability of the interface system. There have been variations in the zeta potential based on changes in the pH, the concentration of ions, temperature, and rock mineralogy [159].

Zeta potential measurements require the core samples to be crushed to powder form. The crushed powder is mixed with brine to form a brine/mineral suspension. A zeta potential analyser (in form of a probe) is used to take the varied potential measurements created by the emulsion for either case. The mode of measurement has mostly been based on the concept of electrophoretic mobility. Some investigations have considered the alteration of wettability on carbonate surfaces on the variation of brine concentration [18,69,160,161].

In some cases, the measurement of zeta potential was based on the resistivity measurements of a consolidated carbonate core saturated with electrolytes of varying concentrations and subjected to streaming potential measurements [162,163]. The streaming potential phenomenon is associated with the generation of an electric field when a liquid is forced to flow past a stationary charged surface. Zeta potential measurements of intact carbonate samples under reservoir conditions were conducted by Alroudhan and Jackson [164]. They used the streaming potential measurements to determine the zeta potential of a calcite sample under varied low salinity brines and oil. Their results provided an understanding of the impact of total salinity and concentration of the potential determining ions (PDIs) on the in-situ wettability. Recently, Collini et al. [165] conducted an integrated controlled salinity water flooding (CSW) where zeta potential measurement was made to understand the improved recovery under reservoir conditions for a carbonate sample. Their results indicated that the magnitude and repulsive zeta potential (derived from the streaming potential) showed a positive correlation with wettability alteration and improved recovery, hence an optimum brine salinity was proposed.

3.3.2. Surface complexation modelling

Wettability indication in carbonate rocks can be examined accurately using surface complexation modelling. This model tends to quantify the electrostatic adhesion which can be used to understand oil recovery in carbonate rocks. The surface complexation model (SCM) describes the equilibrium state of the ion surface chemical reactions of the mineral-solutions interface that gives rise to surface complexes. The results of SCM provides an insight into the surface charge distribution with regards to ion adsorption and determination of surface potential. This is normally achieved via the consideration of inner or outer-sphere surface complexes which are then fitted to adsorption data to discriminate between adsorption mechanisms [166].

As an application to wettability studies in carbonate formations, SCM has been used to study the electrokinetics on calcite-brine and calcite—oil interfaces with variations in the brine compositions, with and without alkalis [167]. Results of the model predictions agreed with the experimental zeta potential measurements. An independently-derived diffuse layer model was developed by Brady and Thyne [155] to determine the adhesive forces by indirectly adsorbing oil on the calcite mineral surface. The results of the model predictions were able to explain the pH shift, plateau of incremental oil production, and oxyanion role in increased oil recovery from carbonates observed in low salinity core floods.

A double layer complexation model was developed by Song et al. [168] to predict the zeta potentials in brines with mixed PDIs (Ca^{2+}, CO_3^{2-}, Mg^{2+}, SO_4^{2-}) to characterise the wettability of synthetic calcite. The model prediction reveals that a positive calcite surface for all brine combinations and PDIs. Also, a significant sensitivity of the calcite zeta potential was observed under CO_2 partial pressures in the various brines. More so, a charge-distribution-multi-site-complexation (CD-MUSIC) model has also been considered by some investigators [169–171]. Eftekhari et al. [172] concluded that their predictions using the CD-MUSIC developed by Wolthers et al. [169] provided the closest fit to the experimental zeta potential measurements of chalk/brine interface when parameters were slightly modified. They also revealed that there was a negligible effect of clay presence on the adsorption of metal ions on the chalk surface. The effect of the presence of clay on the adsorption of metal ions on the chalk surface is negligible. Most of the SCMs are implemented in PHREEQC which is a widely used software developed by USGS for geological system equilibrium calculation. SCM has proven to be a fast, cheap, and versatile tool for understanding the rock-fluids interactions during wettability estimation. However, most of the models cannot be used at high reservoir temperature since they have been calibrated to the adsorption ions of pure crystalline carbonate particles at room temperature.

3.4. Summary

Varied studies have been conducted based on the standard methods using calcite, chalk and dolomite samples [29,90,173,174]. The discussed standard methods of wettability measurement provide surface wettability measurements (in the case of contact angle measurement) and average wettability (in case of AHM and USBM), hence cannot be used to monitor changes in wettability in real-time, such as changes in fluid composition in dynamic conditions. The contact angle method assumes that the rock is chemically homogenous with a topographically smooth surface. This does not apply to reservoir rocks. More so, the pore structural aspects such as mineral heterogeneity, surface roughness, pore topology are not captured in the measurements. Thus, the poor understanding of wettability alteration in most carbonate rocks. These tests are rather conducted under steady-state conditions where initial and final conditions after perceived variations of the rock wettability can be determined at a time. The Amott-Harvey test and USBM are relatively slow, expensive, and labour intensive with contact angle measurement made on surfaces with simple or pure fluids. Albeit these limitations, the standard methods provide a quantitative measure of the inferred wettability, forming a standardised method for comparison with other methods. The need for real-time measurements given the complexity of wettability alteration in carbonates rocks needs attention. The novel methods tend to address this situation to an extent.

The novel techniques though mainly qualitative inferences of wettability provide vital information on the dynamics of wettability changes. The microscopic methods and micro-CT methods provide a pore-scale wettability in real-time and residual state of the rock surfaces. SEM and AFM provide images that capture changes in the rock surface at high resolution. These imaging techniques are far expensive compared to the conventional methods which could be a significant downside. TGA presents adsorption mechanisms that are important for wettability studies in carbonate rock. However, it is a destructive method given the heating involved with samples. Other techniques such as the Zeta potential focuses on the surface chemistry of the solid-fluid interface also provide an inference of carbonate rock wettability based on the surface charge. Zeta potential measurements are mostly conducted in the lab on crushed samples, which does not include the topology of the pore structures. This limitation has been overcome by the consideration of streaming potential (SP) measurements that also indicate zeta potential or surface changes on the brine-mineral and oil interfaces. The use of SCMs as a simulation tool to predict surface charges that indicate wettability alterations on carbonate rocks presents a significant contribution as well. New and improved thermodynamic models need to be developed to incorporate the adsorption ion parameters under reservoir conditions to aid the accuracy of prediction.

Based on the advantages and current limitations of the discussed wettability techniques, it is recommended that a holistic approach be considered in characterising wettability in carbonate rocks under LSWF conditions. This approach will include the integration of sub pore, pore, core and field length scales to fully understand the impact of low salinity on wettability alteration and overall recovery.

4. Concluding remarks

This review puts together numerical and experimental evidence to demonstrate that wettability alteration in carbonates is the driving force for improved oil recovery for the low salinity waterflooding process. Due to the complex nature of carbonates, an in-depth analysis of fluid/fluid and fluid/mineral interactions is necessary to design the optimal formulation that can promote increased oil recovery. Based on the review, the proposed underlying mechanisms (multicomponent ion exchange, electric double layer expansion and mineral dissolution) are responsible for generating the resultant wettability alteration of carbonates from oil/water wet. All these mechanisms can occur in the petroleum reservoir except mineral dissolution due to equilibration. Hence mineral dissolution is considered a secondary mechanism.

The success of LSWF in carbonates depends on several factors such as the oil type, rock mineralogy, pH, salinity/ion concentration and temperature. The presence of anhydrite in certain carbonate rocks influences the carbonate rock response to either ion tuning or salinity reduction in LSWF. The acid/base content influences the adsorption and desorption of the oil materials present in the oil on the rock surface. Thus, affecting the wettability. Other factors such as asphaltene content should be considered in characterising oil samples as the acid/base number measurement is insufficient to understand the oil effect on wettability alteration. The concentration of the PDI's and the temperature are very crucial to trigger the multicomponent ion exchange and electric double layer expansion mechanisms. It is agreed that at high temperatures, the potential determining ions are activated and the exchange of ions at the interface causes the release of oil from the surface of the rock.

For carbonate wettability measurement, the conventional methods are the most used, although they are plagued with measurement limitations. The consideration of novel techniques and surface modelling has provided vital revelations of the mechanisms of wettability alteration in carbonates. To fully describe these mechanisms, a combination of pore-scale experimental and numerical simulations across variable geochemistry and multiscale conditions are required for future investigations.

Abbreviations

LSWF	Low salinity water flooding
EOR	Enhanced oil recovery
MIE	Multicomponent ion exchange
EDL	Electric dielectric layer
NMR	Nuclear magnetic resonance

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