Oil/Water/Rock Wettability: Influencing Factors and Implications for Low Salinity Water Flooding in Carbonate Reservoirs

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Abstract

Wettability of the oil/brine/rock system is an essential petro-physical parameter which governs subsurface multiphase flow behaviour and the distribution of fluids, thus directly affecting oil recovery. Recent studies [1-3] show that manipulation of injected brine composition can enhance oil recovery by shifting wettability from oil-wet to water-wet. However, what factor(s) control system wettability has not been completely elucidated due to incomplete understanding of the geochemical system. To isolate and identify the key factors at play we used SO_4^{2}—free solutions to examine the effect of salinity (formation brine/FB, 10 times diluted formation brine/10dFB, and 100 times diluted formation brine/100dFB) on the contact angle of oil droplets at the surface of calcite. We then compared contact angle results with predictions of surface complexation by low salinity water using PHREEQC software.

We demonstrate that the conventional dilution approach likely triggers an oil-wet system at low pH, which may explain why the low salinity water EOR-effect is not always observed by injecting low salinity water in carbonated reservoirs. pH plays a fundamental role in the surface chemistry of oil/brine interfaces, and wettability. Our contact angle results show that formation brine triggered a strong water-wet system (35°) at pH 2.55, yet 100 times diluted formation brine led to a strongly oil-wet system (contact angle=175°) at pH 5.68. Surface complexation modelling correctly predicted the wettability trend with salinity; the bond product sum ($[>CaOH_2^+][-COO^-] + [>CO_3^-][-NH^+] + [>CO_3^-][-COOCa^+]$) increased with decreasing salinity. At pH < 6 dilution likely makes the calcite surface oil-wet, particularly for crude oils with high base number. Yet, dilution probably causes water wetness at pH > 7 for crude oils with high acid number.

Keywords

Low salinity water flooding, Carbonate reservoirs, Wettability, Contact angle, Surface complexation modelling

Introduction

Carbonates rock host most of the world's oil reserves (> 60 %) [4], which are composed primarily of the minerals calcite and dolomite together with impurities, e.g., quartz, anhydrite, clay minerals, organic matter, and apatite [5]. However, average recovery typically is lower than 40%. Cost-effective and environmentally friendly techniques to enhance oil recovery from carbonates are therefore of broad scientific interest [6]. One such technique that has gained interest is to modify the injected water chemistry to shift reservoir wettability from oil-wet to water-wet in a process termed low salinity water flooding, which is also called *LoSal* flooding by BP [7, 8], *Smart Water* flooding by its originators, Austad and co-workers, at the University of Stavanger, Saudi Aramco[9], and *Designer Water flooding* by Shell [10, 11].

Several mechanisms have been proposed to describe how the approach improves oil recovery in sandstones: fines mobilization [12], limited release of mixed-wet particles [12], increased pH and reduced IFT similar to the alkaline flooding [13], multi-component ion exchange (MIE) [8, 14-16], electrical double layer expansion [17-19], salt-in effect [20], salting-out effect [21] and osmotic pressure [22].

The low salinity water effect in carbonate reservoirs is less clear, which limits application of low salinity water in carbonated reservoirs [1]. Previous studies suggest that wettability alteration is the main mechanism for the low salinity water effect in carbonated reservoirs, despite the fact that the specific factors controlling wettability have not been completely elucidated. For example, most reports suggest that low salinity water shifts reservoir wettability from oil-wet towards water-wet, lifting oil films off the pore surface, whereas Al-Attar, etc. found the opposite [23], arguing that low salinity water shifted reservoir wettability from water-wet to intermediate wetting, thereby increasing recovery. Sulphate apparently acts as a catalyst by adsorbing at pore surfaces more strongly than oil carboxylate groups, thereby changing the rock surface charge locally from positive to negative, and causing repulsion between oil carboxylate groups and pore surfaces [24]. As a consequence, reservoir rock wettability will be shifted from oil-wet to water-wet, thereby increasing oil recovery. However, there is still uncertainty about the nature of wettability change, with some reports suggesting it is double layer expansion [6, 25, 26], and others suggesting it is mineral dissolution [27] and surface complexation [28, 29]. For example, Mahani et al. reported that contact angles was decreased by 5-17^o as high salinity fromation brine was switched over to sea water after 40 hours, which can be interpreted by surface complexation modelling. For example, as pH above 6 at the oil/brine interface, $–COO^-$ increases and $–COOCa^+$ decreases in sea water compared to formation brine because of the decrease of the Ca^{2+}, thereby $–COO^-$ dominates the surface charges at the oil/brine interface. At brine/calcite surface, much more $>CaSO_4^-$ would be generated in the presence of sea water simply because the concentration of SO_4^{2-} in sea water was 14 times higher than that of in the formation brine (e.g., 234 mg/l in FB, 3384 mg/l in SW),. As a consequence, the repulsive force between the oil/brine and brine/calcite increases, shifting the wettability toward more water-wet in the sea water. Note: the pH from Mahani et al.'s test for the fluids before and after the contact angle test did not change (pH for FW=6.9, and pH for SW=8.0).

In addition to salinity, pH also affects the interaction of oil/brine/rock system, thus wettability. For example, Austad et al. hypothesized that low salinity likely triggers a substitution of Ca^{2+} by H^+ for compensating the desorption of cations from clay surfaces [30]. This hypothesis explains why low salinity water usually leads to a local pH increase. Low salinity water also likely facilitates the ion exchange between the embedded Na in phyllosilicate and H^+ [31], thus causing a local pH increase. However, quantitative work remains to be made to understand the pH effect on the interaction of oil/brine/rock.

We thus aimed to gain a deeper understanding of the factors governing the wettability of the oil/brine/carbonate system with a combination of approaches (e.g., contact angle test, surface complexation modelling). Given that the conventional dilution approach is widely used in field, to understand the general effect of water chemistries on low salinity effect in carbonate reservoirs, we removed potential determining ion, SO_4^{2-} and explored the effect of pH, salinity as a whole on wettability of the oil/brine/carbonate system.

We examined the effect of salinity level (formation brine/FB with salinity level at 252,244 ppm, 10 times diluted formation brine/10dFB, and 100 times diluted formation brine/100dFB), on contact angles of oil droplets at the surface of carbonates. To gain a deeper understanding of the geochemical reactions controlling the contact angle results, we used the geochemical speciation code PHREEQC (Parkhurst et al., 1999) to examine the impacts of calcite dissolution and surface complexation.

Rock Mineralogy

Rock mineralogy is essential to wettability alteration in carbonated reservoirs. X-ray diffraction (XRD) of rock samples used in the contact angle measurements showed 98.1 % calcite, 0.7% quartz, and 1.2% ankerite, but no detectable anhydrite ($CaSO_4$).

Brine Properties

To specifically focus on the salinity effect on system wettability, we removed SO_4^{2-} from all of the experimental brines. Formation brine (FB) was synthesised based on the composition of produced water from North Rumaila field having a salinity of 286,677 ppm [32]. Formation brine was then diluted by 10 times (10dFB) and 100 times using deionized water, to obtain low salinity brine (Table 1).

Table 1: Composition of the brines used in contact angle measurements.

Brine	mg/L						TDS (ppm)	pH
	Na^+	Ca^{2+}	Mg^{2+}	K^+	Fe^{2+}	Cl^-		
Formation brine	74638	15200	4526	2013	303	155564	252244	2.55
10dFB	7463.8	1520	452.6	201.3	30.3	15556.4	25224.4	4.42
100dFB	746.4	152.0	45.3	20.1	3.0	1555.6	2522.4	5.68

Note that the brines used in this study had low pH values (Table 1) due to the reaction of Iron(II) chloride ($FeCl_2$) in water, which resulted in formation of ferrous, and chloride ions. This process resulted in the removal of hydroxyl ions from the solution, leaving hydrogen ions in excess, which made the solution acidic.

Experimental Crude Oil

The experimental crude oil was extracted from Stag field located in Commonwealth waters on the North West shelf of Western Australia. To avoid the precipitation and plugging by particulates in the crude oil during injection of crude oil, the crude oil was filtered using 12-micron paper filter. The properties of the crude oil are given in Table 2. Note: the experimental oil had a higher base number (1.02 mg KOH/g) than acid number (0.50 mg KOH/g), suggesting that concentration of $–NH_2^+$ at oil surface may be two times greater than $–COO^-$ [29]. This implies that the bond between carbonate and amine group, $[>CO_3^-][-NH^+]$, may play an important role in system wettability.

Table 2: Properties of crude oil

Property	Unit	Result
density	g/cm^3	0.94
API gravity	°API	18.50
Specific Gravity 260/60°F	-	0.94
Acid number	mg KOH/g	0.50
Base number	mg KOH/g	1.02
Kinematic viscosity @ 20°C	cSt	122.50
Kinematic viscosity @ 40°C	cSt	37.26
Asphaltene content	% mass	0.14
Water content	% volume	0.15
Wax content	% mass	<5

Contact Angle Test

To investigate the effect of water chemistry on wettability of carbonate, we tested the contact angle on the rock with crude oil and aqueous ionic solutions using Vinci IFT-700 (Figure 1). The experimental temperature and pressure was at 60 °C and 2000 psi, respectively. Contact angle tests were conducted using the sessile droplet method. Note: all of the contact angle results were recorded after equilibrium was reached, i.e. the contact angle did not change over 48 hours. Also note that while the substrate roughness, contact angle hysteriss, and preparation procedure all may affect the the macroscopoic contact angle [26], the philosophy of the contact angle test in this study was to highlight the actual trend of the contact angle with salinity rather than the exact initial value of the contact angle.

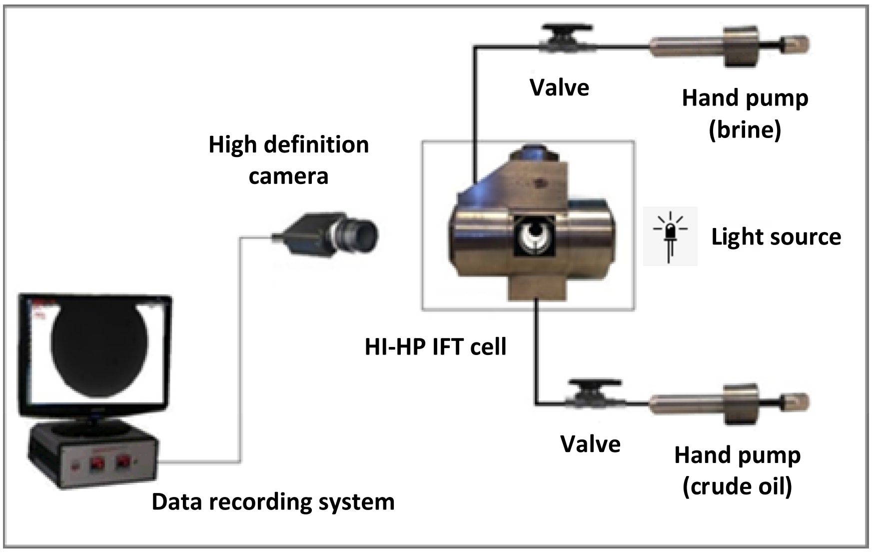

Figure 1: Schematic of contact angle and interfacial tension apparatus.

To obtain representative contact angles, the rock substrates were exposed to air plasma for 10 min to remove organic surface contamination [33]. Note that the aged sample were obtained by putting a clean sample in a beaker with crude oil in an oven at 60 °C for eight weeks to restore wettability. After completing the aging process, samples were dried in the oven and cleaned for 15 min in an air plasma for the second time before measuring the contact angle. Subsequently, the substrates were placed in the HT-HP cell and vacuumed before the cell was filled with brine. Temperature and pressure was set at 60 °C and 2000 psi, respectively. After a state of equilibrium was achieved in the system (constant pressure and temperature), a drop of crude oil (0.04 - 0.06 ml) was introduced through a 0.6 mm diameter needle at the bottom of the cell into the brine environment. Then the droplet was released from the needle and placed on the substrate to measure the contact angle.

Results and Discussion

Effect of Water Chemistry on Contact Angle

The contact angle between oil and the carbonate substrate increased with decreasing salinity, implying that dilution shifts the wettability of oil/brine/carbonate towards more oil-wet. This may explain why the dilution approach does not always trigger low salinity water EOR-effect. For example, the contact angle on un-aged carbonate substrate increased from 30 to 81° with decreasing salinity from FB to 100dFB (Figure 3). A similar trend was also observed with aged carbonate substrate; the contact angle shifted from 35 to 175 ° with decreasing the salinity level from FB to 100dFB.

Although we observed a similar trend in contact angle alteration for both aged and un-aged rock samples, the effect of reduction in salinity on wettability was much more profound on aged substrate compared to un-aged substrate. Our results are in line with Al-Attar et al. [34] who reported that the contact angle increased with the decrease in the salinity level. For example, they observed the contact angle increased from 45° in the presence of FB (197,000 ppm), to 70° when salinity was reduced to 1,000 ppm. They also argue that a shift in carbonate wettability from water wet to intermediate condition triggered incremental oil recovery. Similar results were reported by Mohsenzadeh et al. [35] who found that dilution led to oil-wetting. Successive dilution of FB increased the contact angle from 63° in FB (203,000 ppm), to 130° in 20dFB, shifting wettability from water-wet to oil-wet. However, the literature results also provides examples of the opposite behavior, low salinity brine shifting wettability of carbonate rocks from oil-wet to preferentially water-wet [26, 36-38].

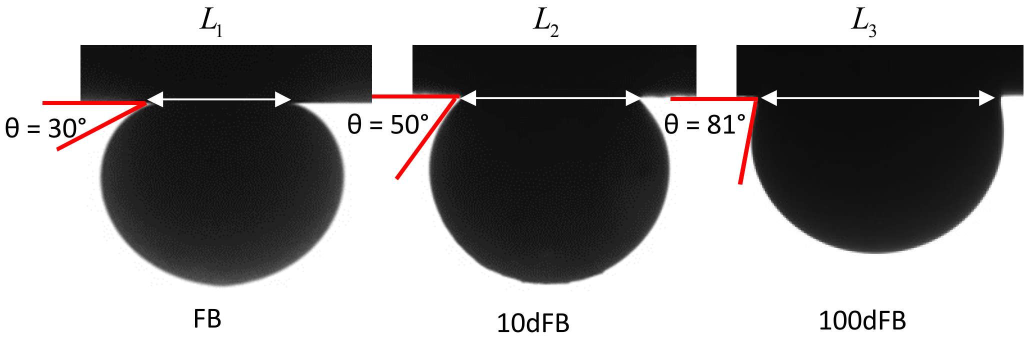

Figure 2: Contact angle of various brine and oil on the un-aged carbonate sample.

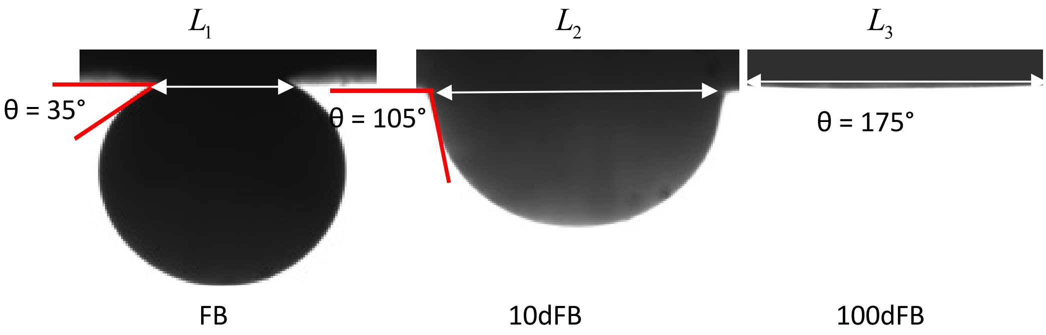

Figure 3: Contact angle of various salinity level and oil on the aged carbonate sample. Note that L means the diameter of the oil droplet on the surface of the calcite, which is an indication of the affinity of the oil phase on the surface of calcite. The greater L is, the system is more oil-wet [26]. (Note: the initial pH of the FB, 10dFB, and 100dFB was 2.55, 4.42, and 5.68, respectively, see Table 1)

Aged samples gave a greater contact angle compared to unaged samples in the presence of given brine. For example, contact angle of aged sample and unaged sample in the presence of 10dFB were 50^{o} and 105^{o}, respectively, in line with Ramanathan et al. [39] who show that aged system became more oil-wet relative to the wetting state of the unaged system. Contact angle measurements have been identified to be the best approach to determine the system wettability [39], which depends on the crude oil compositions (acid number and base number), brine composition, aging and initial water saturation [40]. Aging experimental rock have shown to modify the wettability of oil/brine/rock system due to the adsorption of polar oil components on the rock surface via electrostatic and physiochemical forces [41], although how the aging process affects the controlling factors of the adsorption of polar oil is still open for discussion. However, we believe that combining both electrostatic and non-electrostatic physiosorption together with competitive ion chemisorption (ion exchange and surface complexation) might help to gain a deeper understanding.”

Surface Complexation Modelling

The surface complexation model developed by Brady et al. [29, 42] was applied to calculate the number of charged species that are thought to cause local adhesion of the oil/brine interface to the brine/calcite interface, hence wetting. The bond product sum counts the number of electrostatic connections between the two. Surface complexation modelling (and DLVO theory) presumes an electric double layer at each interface and the existence of charged surface species whose concentrations depend upon the chemical makeup of the water and the oil and mineral surface [43]. In the surface complexation model, the calcite surface area was assumed as 10 m^2/g with site density of 10 μmol/m^2 [29]. The chemical reactions on the surface of calcite can be described by the following reactions (Table 1). We used 25^{o}C Log K for all of the chemical reactions in Table 3 because water chemistry dominates the surface complexation of the oil/brine/rock system and temperature plays a secondary effect [43]. The surface species concentrations were calculated using PHREEQC version 3.3.9 (Parkhurst and Appelo 2013) and a diffuse layer surface model.

Table 3 Surface complexation model input parameters [27, 29, 44, 45]

Interface	Reaction	Log $K_{25^{o}C}$	Reaction
oil/brine	$-NH^+ = -N + H^+$	-6.0	1
	$-COOH = -COO^- + H^+$	-5.0	2
	$-COOH + Ca^{2+} = -COOCa^+ + H^+$	-3.8	3
calcite/brine	$>CaOH + H^+ = >CaOH_2^+$	11.85	4
	$>CaOH + HCO_3^- = >CaCO_3^- + H_2O$	5.8	5
	$>CaOH_2^+ + SO_4^{2-} = >CaSO_4^- + H_2O$	2.1	6
	$>CO_3H = >CO_3^- + H^+$	-5.1	7
	$>CO_3H + Ca^{2+} = >CO_3Ca^+ + H^+$	-2.6	8
	$>CO_3H + Mg^{2+} = >CO_3Mg^+ + H^+$	-2.6	9

Where “>” denotes a site on the carbonate surface while “-” denotes a site on the oil surface.

Effect of Salinity on Number of Oil/Brine Surface Species

Salinity level strongly affected the calculated number of surface chemical groups at the oil/brine interface at a given pH (Figure 4). Note: the site density (Figure 4 and 5) and the number of surface species have the same physical meaning, showing the number of sites (surface species) at the surface of oil/brine and brine/rock. For example, the number of $-NH^+$ groups increased with increasing salinity at low pH (<5.5), yet at pH>5.5, the number of $–NH^+$ groups decreased with increasing salinity. The same trend was predicted by Brady et al. [29] who showed that the calculated number of $–NH^+$ oil groups increases sharply with increasing NaCl, whereas the number of $–NH^+$ groups decreases slightly with increasing the salinity level for a BN/AN = 10 oil at 100 ^oC. They also reported that for pH < 5.7, oil surface charge is dominated by $–NH^+$ groups, showing that increasing ionic strength increases the number of $–NH^+$ groups at the oil/brine interface, attributing it to $–NH^+$ surface activity coefficient increases with salinity [31].

pH also strongly affected the number of oil/brine surface species due to the protonation and deprotonation at surface of oil/brine (see Reaction 1, 2 and 3). For instance, the number of $–NH^+$ species decreased sharply with increasing pH particularly at pH < 6.5 (Reaction 1). Figure 4 also shows that the effect of pH on the concentration of $–NH^+$ groups was much more pronounced than the effect of salinity. Increasing pH also increases the calculated number of $–COOCa^+$ groups (Reaction 3). Yet, the numbers of all of the surface chemical groups ($–COOCa^+$, $–COO^-$, and $–NH^+$) remained constant at pH > 8 (Figure 4).

Our results imply that $–NH^+$ dominates the surface charges at low pH level (pH < 5.5), whereas $–COOCa^+$ and $–COO^-$ govern oil surface chemistry at pH > 6. Therefore, we believe that the dilution likely triggers oil-wet system at low pH < 5.5, particularly for crude oils with high base number. Dilution probably leads to water-wetting at for crude oils with high acid number at pH > 7.

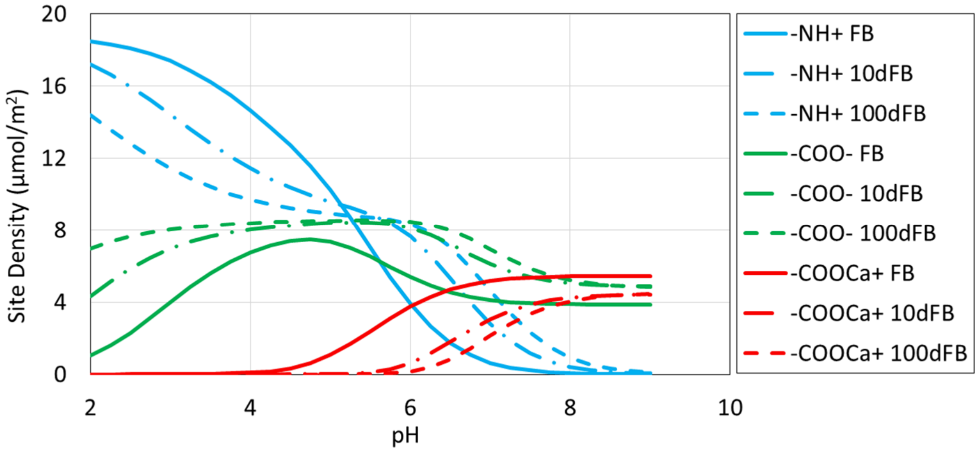

Figure 4. Number of oil surface chemical groups versus pH and dilution.

Effect of Salinity on Number of Rock/Brine Surface Species

To understand oil/brine/carbonate wettability we must characterize speciation at the brine/carbonate surface. We calculated the number of calcite surface species as a function of salinity and pH. We found that salinity strongly affected the number of $>CO_3^{2-}$ and $>CO_3Ca^+$ groups at a given pH (Figure 5). For example, the number of $>CO_3^{2-}$ groups was calculated to increase with decreasing salinity at a given pH. However, the number of $>CO_3Ca^+$ groups increases with increasing salinity, and increased Ca^{2+} (Reaction 8). The concentration of $>CO_3Mg^+$, similar to $>CO_3Ca^+$, also increased with increasing salinity (Because the concentration of Mg^{2+} in each of the brines was 2 times less than that of Ca^{2+}, the variation of the $>CO_3Mg^+$ with pH was not shown in Figure 5). Similar results were reported by Mahani et al. [28] who showed that the surface concentration of $>CO_3Mg^+$ decreased with decreasing salinity. For example, 100 times diluted seawater prompted a 0.2 µmol/m² decrease in $>CO_3Mg^+$ groups at pH < 8, but the trend of the decrease became more pronounced at pH > 8 owing to Reaction 7 moving to the right at high pH.

Effect pH on number of different surface species on brine/rock surface varies (Figure 5). $>CaOH_2^+$ showed little variation with pH due to the high equilibrium constant (Log K_{25oC}=11.85, Reaction 4). Yet, $>CO_3^-$ and $>CO_3Ca^+$ all witness a dramatic increase with increasing pH from 2 to 6 because of the low equilibrium constant (Log K_{25oC}=-5.1 for $>CO_3^-$, and -2.6 for $>CO_3Ca^+$, Reaction 7 and 8). Note: dilution had a negative impact on the number of the two surface species, showing that number of surface species increased with decreasing salinity. However, in general, pH controls the general trend of the number of surface species. Low pH (<6) renders the Reaction 3 and 4 to shift the left-hand side, leading to low number of surface species. When pH increased to 6, the number of all surface species became stable.

The calculated number of $>CaOH_2^+$ groups was largely insensitive to pH and salinity. The same trend was calculated by Brady et al. [29] who showed that the surface concentration of $>CaOH_2^+$ varied little with pH from 5.3 to 8. Increasing pH increased the calculated number of $>CO_3^-$ groups up to pH ~ 6; pH had less of an effect at higher pH. Figure 5 shows that the effect of salinity on the number of $>CO_3^-$ groups was much greater than the effect of pH.

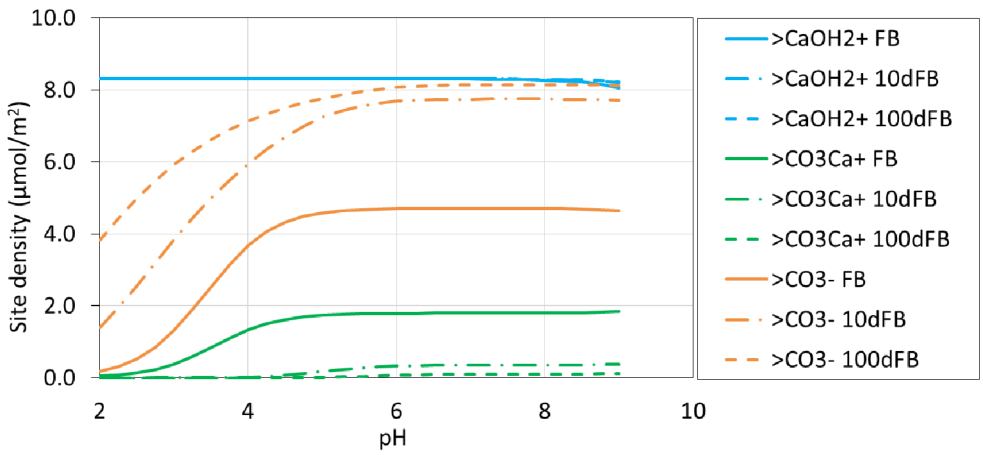

Figure 5. Site density of calcite surface groups versus pH and dilution.

Effect of Salinity on Electrostatic Bridges between Oil and Rock

Oil-wetness is thought to be correlated with the number of electrostatic bonds between oil and rock [29, 46]. We used our calculations above to quantify the number of electrostatic bonds, and wetting, by summing the number of oil/rock electrostatic pairs. For example, the concentration product [>CO$_3^-$][-NH$^+$], is the bond product quantifying the number of electrostatic bonds between oil –NH$^+$ groups and calcite >CO$_3^-$ groups. Salinity level strongly affected the calculated individual bond products, and the bond product sum ([>CO$_3^-$][-NH$^+$] + [>CO$_3^-$][-COOCa$^+$] + [>CaOH$_2^+$][-COO$^-$]). For example, the bond product [>CO$_3^-$][-NH$^+$] increased with decreasing salinity (Figure 6) because the calculated number of >CO$_3^-$ groups increases substantially with decreasing salinity despite -NH$^+$ decreasing with decreasing salinity level at pH < 5.5. The bond product [>CO$_3^-$][-COOCa$^+$] increased with increasing salinity at pH < 7.3, but increased with salinity at pH > 7.3. Each change occurred because of the salinity and pH effects on the number of bond product surface species present at the oil and calcite interface. Given that the experimental oil used in this study had a low acid number, 0.50 mg KOH/g, compared to the base number, 1.02 mg KOH/g, a slight change of [>CO$_3^-$][-COOCa$^+$] bond product did not affect the trend of variation of the bond product sum. The bond product of [>CaOH$_2^+$][-COO$^-$] was tightly controlled by the variation of site density of -COO$^-$ owing to a negligible change of the >CaOH$_2^+$ along with pH and salinity level.

The bond product sum results show that lowering the salinity level triggered greater bond product sum, which varies at a different pH level. This implies that decreasing the salinity level triggers more oil-wet system at a given pH level, explaining why the low salinity water effect was not always observed using the conventional dilution approach. The surface complexation modelling also correctly predicted the wetting characteristic of the oil/brine/calcite system in this study, showing that FB, 10dFB and 100dFB yielded a bond product sum of 29, 136 and 140 (μmol/m^2) ^{2} for the oil/brine/calcite system in line with the contact angel test (Figure 2 and 3). Note: the great the bond product means more oil-wet system. However, our surface complexation modelling raises two questions: why does the aging process affect the wetting characteristics of the oil/brine/calcite system for the same bond product sum predicted by surface complexation modelling, and why did 100dFB exhibit a slight increase in bond product sum compared to 10dFB, but the contact angle increased tremendously? The potential explanation for the discrepancy is that:

In situ pHs during the contact angel test were on the low side due to deprotonation [43] (see Reaction 1-3 and 7-9). Therefore, the in situ pH likely shifted towards left-hand side, which in return gives a greater difference of bond product sum for the 10dFB and 100dFB.

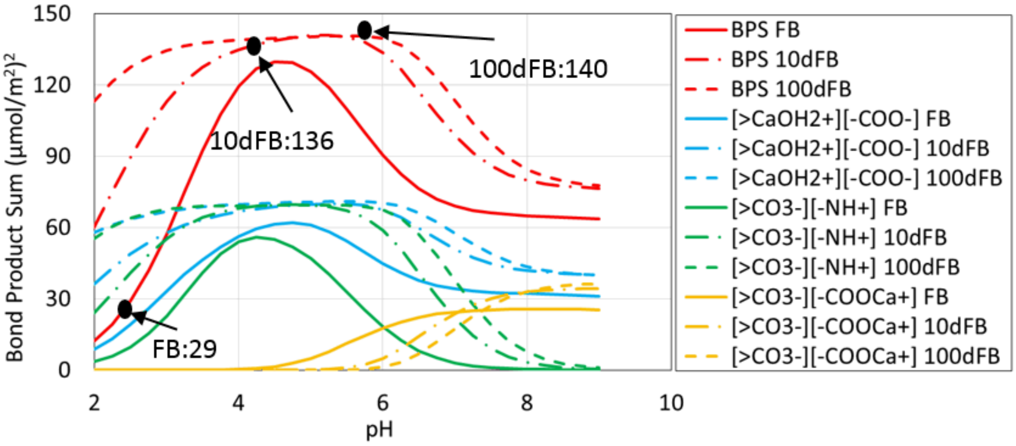

Figure 6 Bond product between the interface of oil/brines and brines/carbonate versus pH.

Implications

Our contact angle and surface complexation modelling both identify that water chemistry, salinity both affect the interaction of the oil/brine and brine/carbonate, yet pH level plays a fundamental role. This is because pH strongly affects surface chemistry of the oil/brine regardless of the magnitude of oil acid number and base number. For a high acid number oil, dilution likely causes low salinity water EOR effect. This is because the functional chemical groups, [$-COO^-$] from oil surface and [$>CO_3^-$] from rock surface, increase with decreasing the salinity, which in return generating repulsive force, thus a more water-wet system. For a high base number oil, the functional chemical group of [$-NH^+$] from oil interface dominates the surface charge of oil interface at low pH level. Moreover, [$>CO_3Ca^+$] favours the high salinity level. Together, a high salinity level renders a water-wet system, which explains why the conventional dilution approach does not always yield an incremental oil recovery compare to formation brine.

We also confirm that low salinity water can shift the wettability with an absence of SO_4^{2-}. In other words, the presence of SO_4^{2-} in the aqueous ionic solution is not necessary to observe the low salinity water EOR effect. This is not because SO_4^{2-} does not affect the surface geochemical reaction, rather it is because the wettability of the system is governed by the water chemistry, pH, salinity level and the oil compositions (acid number and base number) as a whole instead of an individual ion. Therefore, we argue that surface chemical modelling should be applied to screen the potential reservoir candidate, and provide a framework to design the injected water chemistry for a given oil/brine/rock system. Moreover, note that PHREEQC calculations (not described here) point to relatively little calcite dissolution during contact angle measurements in consistent with Nasralla et al. who did a more extensive studies disproving any calcite dissolution link to wettability [47, 48].

Conclusions

Our study demonstrates that the wetting characteristics of oil/brine/calcite system is strongly influenced by the surface chemistry of oil/brine and brine/calcite, which is governed by the composition of crude oil (e.g., acid number and base number), and water chemistry (pH, salinity level and the composition of the aqueous ionic solutions). We used a crude oil with base number (BN=1.02 mg KOH/g) and acid number (AN=0.5 mg KOH/g). We tested the contact angle on aged and un-aged carbonate rocks, with crude oil and aqueous ionic solutions under pressure of 2,000 psi and temperature of 60 °C. We independently calculated the concentrations of charged surface species, and electrostatic bridges between the oil and the calcite.

Formation brine caused a strongly water-wet system (contact angle=35°), yet 100 times diluted formation brine led to a strong oil-wet system (contact angle=175°). The surface complexation modelling correctly predicted the trend of the wetting characteristic in the presence of various salinity level, showing that the bond product sum increased with decreasing salinity. Our results suggest that that at $pH < 6$, all other things being equal, conventional dilution approach likely prompts oil-wetness particularly for the crude oil with high base number. Dilution probably causes water wetness at $pH > 7$ for crude oils with high acid number. In this work, while we did not explicitly convert the bond product sum to the wettability of the system, or the oil recovery in an actual oil reservoir, surface complexation modelling allows us to put boundaries on injected water chemistry, and quantify the key factors governing wetting characteristics of the oil/brine/calcite system.

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