

Novel Application of the Flotation Technique To Measure the Wettability Changes by Ionically Modified Water for Improved Oil Recovery in Carbonates

M. Adeel Sohal,^{*,†} Geoffrey Thyne,[‡] and Erik G. Søgaard[†]

[†]Department of Chemistry and Bio-science, Aalborg University, Esbjerg, Denmark

[‡]ESal, 1938 Harney Street, Laramie, Wyoming 82070, United States

ABSTRACT: The accurate determination of the wetting condition of carbonate reservoirs is a prerequisite for the selection of any enhanced oil recovery (EOR) fluid. Most carbonate formations are initially oil-wet to intermediate-wet at reservoir conditions. In order to correctly choose an EOR fluid to alter the wettability, we need to understand the initial wetting conditions and design an ionically modified water (advanced water) to alter wettability and improve oil recovery. If a reservoir has already been reached to the optimum wetting conditions by injecting formation water or any other fluid, then there is no need for ionically modified water. A number of methods have been devised to identify the wetting conditions including contact angle measurements, spontaneous imbibition, and chromatographic separation, etc. But contact angle measurement requires surfaces that lack natural surface roughness, spontaneous imbibition tests take months, and chromatographic separation is feasible only for core flooding in sulfate free carbonates at low temperature. A novel application of the well-established technique known as flotation was used in this study to measure the oil-wet and water-wet percent of pure biogenic chalk (Dan Chalk from Denmark). It is an accurate, fast, and most reliable method to quantitatively measure the water-wet and oil-wet fractions of a reservoir rock. It determines the potential of advanced water to improve wettability within days, instead of measurements that can take months and require expensive equipment. Using this technique we were able to quantify the wettability alteration caused by low salinity and potential determining anions (PDAs) such as SO_4^{2-} , BO_3^{3-} , and PO_4^{3-} . The wettability data show maximum oil recovery by dilution is coincident with maximum wettability alteration. The experiments also show that the presence of sulfate or borate enhances wettability alteration by dilution. Moreover, the combined and individual effect of potential scale forming ions (Ba^{2+} and Sr^{2+}) on wettability restoration was identified. The effect of interfacial tension (IFT) on the measured wettability alteration and the amount of oil attached to the water-wet percent of rock was also determined.

1. INTRODUCTION

Carbonate reservoirs have been the major target of all types of enhanced oil recovery (EOR) methods due to the generally low recovery factor ($\sim 1/3$ of original oil in place (OOIP)). The causes of this low recovery factor are attributed to the reservoir's complex structure that usually includes abundant natural fractures and the affinity of carbonate surfaces to the oil phase. This attachment or adhesion of the oil phase onto carbonate surfaces is known as oil-wetting. Different types of EOR methods such as surfactant flooding, caustic flooding, ionically modified water, and nanotechnology, etc., have been employed to change or reduce this adhesion. But, currently, the approach of modifying ionic composition and strength of injected water (advanced water) has captured more attention due to low capital investment and operating cost. While a number of experimental studies have shown that changing water chemistry increases oil recovery, scientific interest in advanced waterflooding was stimulated by the historical observation of unexpectedly high oil recoveries from injecting seawater into the fractured Ekofisk chalk reservoir of the North Sea.^{1,2} The fundamental observations from the laboratory and field show that altering water chemistry increases oil mobility under flow and imbibition, which means wettability has been altered. Since that time, a number of research projects have been performed to investigate the recovery mechanisms and

approaches have been to alter ionic composition and/or strength separately or together.

Alteration of ionic composition is based on the idea that the potential determining ions (PDIs) such as Ca^{2+} , Mg^{2+} , SO_4^{2-} , PO_4^{3-} , and BO_3^{3-} react with the carbonate surfaces to improve oil recovery by altering surface charge. It is believed that the trivalent anions from injected water interact with the carbonate surfaces and alter the surface charge. Then divalent cations attach to the released oil acid groups and modified carbonate surfaces by developing different complexes as described by Hiorth et al.,³ Brady et al.,⁴ and Mahani et al.⁵ using surface complexation modeling. Moreover, a number of coreflood and imbibition experiments were performed on Stevns Klint outcrop chalk and Middle Eastern carbonates by Austad et al.,⁶ Strand et al.,⁷ Zhang et al.,^{8,9} and Gupta et al.¹⁰ In these experiments concentrations of PDIs in the effluent were determined by ion chromatography to infer changes in surface chemistry and the shift to more water-wet surfaces.

In the second approach the ionic strength of injected seawater or formation water was decreased to improve the oil recovery. The improved oil recovery was attributed to the expansion and increased stability of the water films between

Received: April 27, 2016

Revised: July 13, 2016

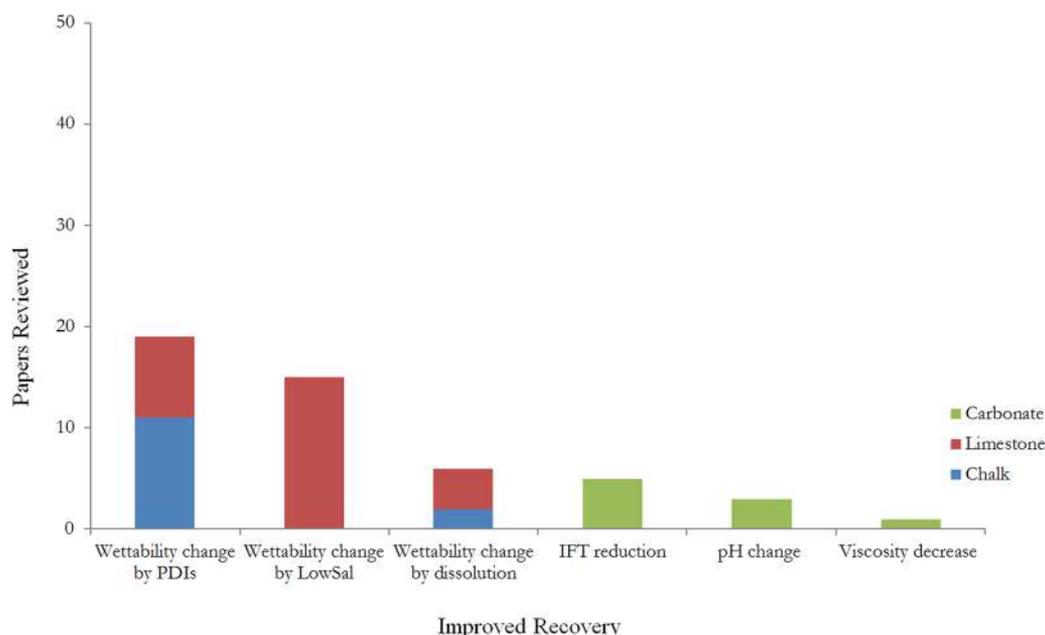


Figure 1. Proposed oil recovery mechanisms, showing current research trend, by ionically modified water in carbonate reservoirs.¹⁹

solid and oleic phases, although the mechanism is less clear. Most of the low salinity water experiments were conducted on Middle Eastern carbonates by Yousef et al.,¹¹ Al Harrasi et al.,¹² Zhang and Sarma,¹³ Al-Attar et al.,¹⁴ and Alameri et al.¹⁵ to improve recovery. Al-Shalabi et al.^{16,17} used a geochemical flow and transport model to determine that electrical double layer (EDL) expansion did not contribute to the water relative permeability change and suggested that changing the surface charge of carbonates was the dominant wettability alteration process as a result of low salinity water (LSW). This proposed mechanism was also cited by Mahani et al.¹⁸ based on experimental measurements of ζ potential.

1.1. Contributing Recovery Mechanisms. According to Sohal et al.¹⁹ the dominant oil recovery mechanisms proposed in current research are as follows: (a) wettability alteration, (b) IFT reduction, and (c) viscosity decrease as shown in Figure 1. Wettability for petroleum engineers is defined as the relative ease of flow for the oil and water phases in porous media. If oil and water are equally mobile, the systems' wettability has a value of zero on the Harvey–Amott scale. The described different effects which caused wettability alteration (PDIs, LowSal, and rock dissolution) have been experimentally investigated as well as modeled in the published literature. But there has still been a lack of detailed studies to differentiate the contribution of each mechanism in the observed wettability. We have tried to fill this gap with our experimental study. A novel application of flotation was employed to identify these vital relationships and to verify the contribution of each parameter to wettability change.

1.2. Flotation Experiments. Flotation has been routinely used for over a century for separation of suspended mineral particles.²⁰ The technique depends on the difference in surface wettability of valuable versus waste minerals to physically separate mineral suspensions. In aqueous solutions, mineral particles with weak adhesion to water (oil-wet or hydrophobic) can remain in suspension or float, while particles with strong adhesion to water (water-wet or hydrophilic) will sink.²¹ This method allows valuable mineral grains to float while unwanted grains sink. Modern practice includes the formation of froth

and sorption of organic material to mineral grains to increase hydrophobic surface area and promote flotation.²²

In the field of petroleum engineering flotation technique was initially applied as a bottle test by Dubey and Doe²³ to investigate the effect of acid and base numbers of crude oil on wetting characteristics. They used single salt component brine (0.02 M NaCl) and 60–120 mesh silica powder and varied the pH value from 2.1 to 9.1 in their room temperature experiments to qualitatively measure wetting. Later, Wu et al.²⁴ used this method to test the wettability reversal by surfactant solution in carbonates with minor modification and named it flotation test. The method was adapted by Mwangi et al.²⁵ to study the effect of rock mineralogy (Austin chalk, Indiana limestone, Silurian dolomite, and Berea sandstone), aqueous chemistry (salinity), surface active compounds, and temperature. They used decane as an oleic phase in their experiments. This modified flotation test (MFT) proved a successful quantitative technique to rapidly test the influence of oil and brine chemistry on wettability on sandstone and carbonate reservoir material at different temperatures. The method can also serve as a screening tool to estimate the wettability alteration potential of brines in a quick time frame and with high repeatability and is an excellent process to differentiate the impact of PDIs and low salinity on wettability alteration that is hard to measure otherwise.

In this study the effect of ionic strength and composition of brine on chalk wettability has been investigated at 23 and 100 °C using the modified flotation technique. The contribution of ionic strength and ionic composition as well as the role of potential scale forming ions (Ba^{2+} and Sr^{2+}) in wettability alteration and restoration were investigated. The correlation between IFT and wettability was also investigated. In addition, the method allowed measurement of the amount of oil that remained attached to water-wet surfaces after wettability alteration.

2. MATERIAL AND METHODS

2.1. Rock Material. In this study outcrop Dan chalk material was taken from Dankalk A/S, Denmark. The elemental composition of the

chalk material was measured by X-ray fluorescence (XRF) technique using Lab-X 3000 XRF equipment from Oxford instruments. The elemental composition of Dan chalk converted into oxides and has been given in Table 1. Total CO₃ refers to the total carbonates in the

Table 1. XRF Analysis of Outcrop Dan Chalk

species	%
CaCO ₃	96.2
SiO ₂	1.25
Al ₂ O ₃	0.17
MgCO ₃	0.54
total CO ₃	96.74

above-described analysis, in this case comprised of Ca and Mg carbonate. The chalk samples were dried at 100 °C for several days and ground with a ball mill, sieved to mesh size between 50 and 100 μm, and preserved in a glass jar. A minor amount of smaller grain size may be found in the sieved material. A sample of chalk powder was dried at 100 °C for several days to verify the moisture content, which was almost zero. Therefore, the mass of 1.0 g of sample represents pure chalk.

2.2. Brines. The synthetic brines were prepared by mixing reagent grade salts in deionized water (DIW). In the brine preparation process a practical approach was adopted so that the prepared brines would be relevant to real field cases. The compositions of all of the synthetic brines were taken from the published literature and encompassed formation water (FW) and seawater (SW). All of the brines contain divalent ions that are found in carbonate reservoirs. The compositions, ionic strength, total dissolved solids (TDS), and densities of all of the different brines are listed in Table 2. The densities of prepared brines were measured by DMA 35 Anton Paar density meter at room temperature. FW with potential scale forming ions such as Sr²⁺ and Ba²⁺ was included. All of the diluted versions of SW were prepared by adding deionized water. The molar concentration of borate anion is a bit less than that of sulfate (SO₄²⁻) in SW. The smaller concentration of borate was used due to precipitation observed at room temperature for higher concentrations. The prefix D with a numeric value represents times of dilution of original brine whereas VB, EFW, B, and S represents Valhal FW, Ekofisk FW, borate, and sulfate, respectively.

2.3. Crude Oil. Stock tank crude oil from a chalk reservoir of the Danish North Sea sector was used in this experimental study. The oil was centrifuged at 3800 rpm for 1 h to remove the solid particles and water. The acid number (AN) and base number (BN) of crude oil characterize the polar components that develop adhesion to the rock surface. These components are neutralized by a strong base or acid and then calculated by the consumed quantity of acid or base. In this study potentiometric titration method is used to calculate these numbers with a TitroLab 90 instrument from Radiometer that consists of a control unit TIM 90 (pH meter), buret station ABU 900, and sample still SAM 7. The titration method was initially developed by Dubey and Doe²³ and then revisited by Fan and Buckley.²⁶ In this study the potentiometric titration method from Metrohm was used (given in OILPAC collection analysis). The density of crude oil was measured by DMA 35 Anton Paar density meter and viscosity at 25 and 90 °C by PVS rheometer from Brookfield. The crude oil properties are listed in Table 3.

2.4. Interfacial Tension and pH. IFT between all brines and crude oil was measured at room temperature and 90 °C. The pendant drop method was employed with the DSA-100 drop shape analyzer from Krüss, Hamburg, Germany. The denser phase (brine) filled the glass cuvette, and a drop of the lighter phase (oil) was introduced to the brine using a J-shaped needle in a bottom up configuration. IFT is calculated from the shadow image of a pendant drop using drop shape analysis. The shape of the suspended drop is determined by the balance of gravity and surface forces using Laplace's equation. A glass cuvette containing a denser phase was connected to a water bath to increase the temperature up to 90 °C. pH values of the original brine

and effluent were measured by PHM-210 from Radiometer Analytical. The variation of pH is an indication of precipitation or dissolution as well as a possible type of surface charge between the interfaces. The type of charge between the interfaces increases or decreases the disjoining force that is linked to oil adhesion onto the rock surface. The IFT and pH of brines and effluent are given in Table 4.

2.5. Flotation Experiment. In these experiments 1 g of rock sample is aged in 10 mL of brine at 100 °C for a couple of hours and then decanted into another test tube. The brine is collected and preserved in a sealed test tube for pH measurement. Brine-wet grains were aged with 5 mL of crude oil for 24 h at 100 °C and shaken twice a day for a few seconds. After oil aging, the decanted brine is added back into the test tube and gently shaken with the vortex shaker. Then for a couple of hours the mixture is allowed to settle at the same temperature. Finally, floating oil-wet grains are removed and the walls of the test tubes rinsed with DI water to clean any stuck grains. The rinsing step is repeated twice or thrice to remove all the oil-wet grains from the test tube. The precipitated water-wet grains were coated with oil which could not be removed during the rinsing process. So the water-wet oil coated grains were dried and weighed and then washed with a volatile organic solvent to remove the attached oil. The cleaned and dried water-wet grains are subtracted from the original mass to calculate the amount of oil-wet grains.

Experiments were performed to select the best proportions of rock sample, brine, and crude oil as well as aging time, grain size, rinsing, and mixing steps to determine the conditions for optimum results. The final amounts were 5 mL of oil, 10 mL of brine, and 1 g of rock powder. A 1 g amount of rock was chosen as the minimum amount of rock that produced good reproducibility (±5%), while minimizing consumption of the most limited resource, reservoir rock. The minimum amount of rock that produced optimum results was selected for experiments to save resources. A diagram of the experimental setup with major operating steps is shown in Figure 2.

2.5.1. Oil Adhesion and Cleaning. It was observed that a measurable amount of oil was still attached to water-wet grains after the wettability experiments and the amount was different for different advanced fluids. This oil is referred to as retained oil. Some components of crude oil will remain strongly absorbed to the rock and can only be removed by solvent extraction.²⁷ In this study the amount of oil that was attached to water-wet chalk grains after wettability alteration was measured for each type of brine at 100 °C. This amount was measured by the mass difference of washed and dried oil coated water-wet grains from unwashed dried water-wet grains as shown in Figure 3. The oil coated grains were washed by organic solvent without dissolution of chalk grains. It was observed that a measurable amount of oil was still attached to water-wet grains after wettability alteration and the amount was different for different advanced fluids.

3. RESULTS AND DISCUSSION

3.1. Flotation versus Imbibition. The Dans outcrop chalk wettability as determined by flotation and by the chromatographic separation technique imbibition for different brines is compared in Figure 4. The chalk wettability data are taken from the imbibition experiments by Fathi.²⁸ The results from the flotation technique produced very similar trends of wettability alteration with the chalk becoming more water-wet with dilution and added sulfate content. The results show that the flotation technique provides a useful alternative to traditional wettability measurements.

There is a difference in the magnitude of values between the two techniques. This is expected as the temperatures (90 versus 100 °C) and crude oil properties²⁹ used were different. The acid number (AN = 1.90 mg of KOH/g) of crude oil that was used in the imbibition study by Fathi et al.²⁹ was 3 times greater than the AN (0.52 mg of KOH/g) of crude oil which was used in the flotation experiments. The higher polar content of the oil

Table 2. Ionic Composition (mmol/L), Ionic Strength, and Density of All Used Brines

brines	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	Na ⁺	Cl ⁻	HCO ₃ ⁻	K ⁺	Ba ²⁺	Sr ²⁺	[B ₄ O ₅ (OH) ₄] ²⁻	ionic strength (mmol/L)	TDS (g/L)	density (g/cm ³)
VB	29.249	7.870	0.704	995.962	1064.559	8.928	4.695	0.000	0.000	0.000	1112.717	62.798	1.041
EFW	99.922	21.889	0.000	1155.561	1423.306	3.952	7.364	1.842	8.514	0.000	1559.425	83.091	1.056
EFW*0Sr	99.922	21.889	0.000	1155.561	1406.278	3.952	7.364	1.842	0.000	0.000	1533.883	81.742	1.055
EFW*0Ba	99.922	21.889	0.000	1155.561	1419.622	3.952	7.364	0.000	8.514	0.000	1553.899	82.708	1.056
EFW*0(Sr*Ba)	99.922	21.889	0.000	1155.561	1402.594	3.952	7.364	0.000	0.000	0.000	1528.356	81.358	1.055
SW*B*0S	12.992	44.515	0.000	420.446	525.142	2.024	10.060	0.000	0.000	9.177	612.204	32.158	1.021
2D*SW*B*0S	6.496	22.257	0.000	210.223	262.571	1.012	5.030	0.000	0.000	4.589	306.102	16.079	1.009
10D*SW*B*0S	1.299	4.451	0.000	42.045	52.514	0.202	1.006	0.000	0.000	0.918	61.220	3.216	1.000
20D*SW*B*0S	0.650	2.226	0.000	21.022	26.257	0.101	0.503	0.000	0.000	0.459	30.610	1.608	1.000
100D*SW*B*0S	0.130	0.445	0.000	4.204	5.251	0.020	0.101	0.000	0.000	0.092	6.122	0.322	0.998
SW	12.992	44.515	24.007	450.107	525.142	2.024	10.060	0.000	0.000	0.000	656.695	33.392	1.022
2D*SW	6.496	22.257	12.004	225.053	262.571	1.012	5.030	0.000	0.000	0.000	328.347	16.696	1.010
10D*SW	1.299	4.451	2.401	45.011	52.514	0.202	1.006	0.000	0.000	0.000	65.669	3.339	1.000
20D*SW	0.650	2.226	1.200	22.505	26.257	0.101	0.503	0.000	0.000	0.000	32.835	1.670	0.999
100D*SW	0.130	0.445	0.240	4.501	5.251	0.020	0.101	0.000	0.000	0.000	6.567	0.334	0.997
SW*0S	12.992	44.515	0.000	460.443	583.493	2.024	10.060	0.000	0.000	0.000	643.023	33.391	1.022
2D*SW*0S	6.496	22.257	0.000	230.221	291.746	1.012	5.030	0.000	0.000	0.000	321.512	16.696	1.010
10D*SW*0S	1.299	4.451	0.000	46.044	58.349	0.202	1.006	0.000	0.000	0.000	64.302	3.339	1.000
20D*SW*0S	0.650	2.226	0.000	23.022	29.175	0.101	0.503	0.000	0.000	0.000	32.151	1.670	0.999
100D*SW*0S	0.130	0.445	0.000	4.604	5.835	0.020	0.101	0.000	0.000	0.000	6.430	0.334	0.998
SW*0NaCl	12.992	44.515	24.007	50.038	125.074	2.024	10.060	0.000	0.000	0.000	256.626	10.010	1.006
SW*0NaCl*4S	12.992	44.515	96.029	194.082	125.074	2.024	10.060	0.000	0.000	0.000	472.692	20.241	1.012

Table 3. Crude Oil Properties

AN (mg of KOH)/g	BN (mg of KOH)/g	viscosity (mPa·s)		density (g/m ³)
		at 90 °C	at 25 °C	at 25 °C
0.52	1.60	3.48		0.862

used in the imbibition experiments would be expected to create more reaction with the rock surface and thus more change in wettability (more water-wetness) for the same change in chemistry, as is the case.

In addition, the potential for precipitation is rarely accounted for in imbibition experiments especially for brines enriched with potential anions. For instance, at high temperatures sulfate may form anhydrite, decreasing the sulfate concentration and lessening the sulfate contribution to wettability alteration. This effect may not be recognized unless dissolved sulfate is measured during experiments.

Moreover, imbibition experiments require months to collect results whereas the flotation results are collected within days, making this technique much faster than traditional measurements of wettability for reservoir material. Finally, the flotation technique allows physical separation of the portions of reservoir rock that are water-wet from grains that are oil-wet. The technique also allows direct measurement of the portion of oil that is tightly bound (wetting) to water-wet grains and not able to be desorbed by changing water chemistry. This is important since the ultimate goal of wettability alteration by advanced water is to increase recovery and we need to better understand the fraction of oil that can be released by advanced water versus the fraction of oil that remains adhered to the rock.

The results show that the potential for advanced water to change the wettability to more water-wet conditions is related to the initial wettability. This can be seen by comparing the water-wet percents of the same chalk by VB (25%) and EFW (17%) formation waters as shown in Figures 4 and 10, respectively. If the reservoir rock is closer to water-wet conditions, then there is less potential for advanced water to improve water wetness. The same crude oil, chalk material and temperature were used to measure the initial wetting conditions

Oven



Figure 2. Diagram illustrating the flotation experiment procedure. Sunken rock powder is considered water-wet and floating rock powder is oil-wet.

and EFW turned the rock more oil-wet compared to VB. So the composition of water played a vital role to develop the wetting conditions in addition to crude oil properties and reservoir temperature.

3.2. Oil Recovery versus Wettability Alteration. The wettability alteration trend found in flotation experiments follows the amount of additional oil recovered in imbibition and coreflooding experiments as shown in Figures 5 and 6. We cannot directly relate the amount of additional oil recovery to the amount of wettability change. The additional recovery may also be related to other factors such as a decrease in interfacial tension, viscosity, formation of emulsions, and development of oil bank, etc., in addition to wettability alteration. However, the strong relationship between the degree of wettability alteration and increased recovery shows wettability alteration as measured by flotation can be a very useful measure in the prediction of increased recovery.

Table 4. Brines pH, Effluent Average pH at 23 °C, Average Retained Oil, IFT at 23 and 90 °C

brines	IFT (mN/m)		av SOR (g of oil)/(g of rock))	brine pH	effluent av pH
	at 23 °C	at 90 °C			
SW*B*0S	11.465	13.177	0.392	8.74	8.30
2D*SW*B*0S	11.674	13.414	0.430	8.86	7.63
10D*SW*B*0S	12.126	13.493	0.510	8.97	8.17
20D*SW*B*0S	13.484	13.734	0.504	8.85	8.11
100D*SW*B*0S	16.769	14.877	0.522	8.64	8.22
SW	15.518	11.879	0.371	7.93	7.43
2D*SW	17.081	12.224	0.339	8.05	7.66
10D*SW	21.170	14.787	0.317	7.61	7.83
20D*SW	23.160	15.778	0.288	7.35	7.99
100D*SW	23.472	19.006	0.425	7.15	8.08
SW*0S	16.018	12.007	0.420	7.81	7.76
2D*SW*0S	19.774	12.666	0.455	7.63	7.40
10D*SW*0S	22.512	13.256	0.448	7.90	7.81
20D*SW*0S	22.664	16.445	0.512	7.16	7.99
100D*SW*0S	23.275	20.497	0.517	7.34	8.12
SW*0NaCl	15.249		0.400	7.12	7.81
SW*0NaCl*4S	15.040		0.390	6.06	7.63

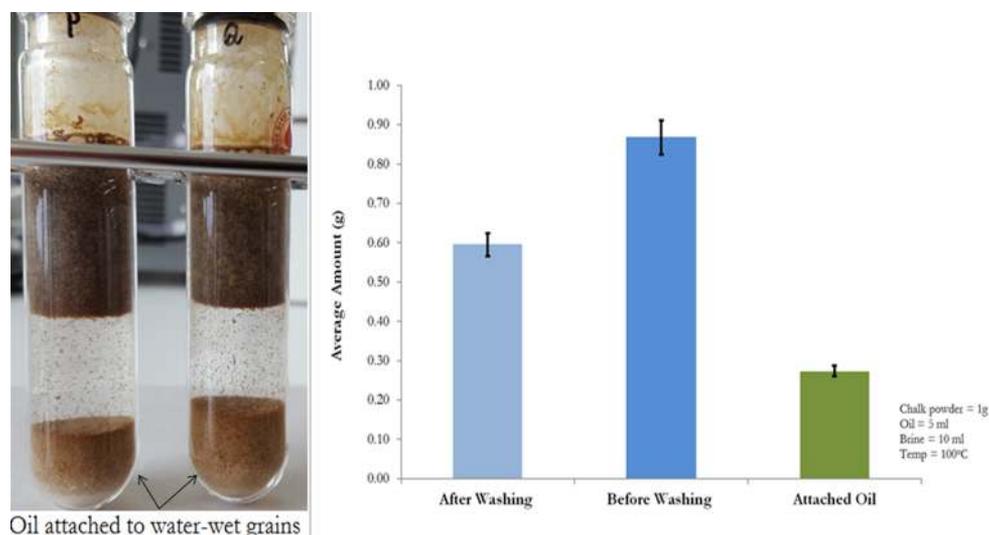


Figure 3. Average amount of Dan chalk water-wet grains before and after washing with organic solvent and amount of oil attached to these grains. Error bars represent $\pm 5\%$, the experimental uncertainty associated with the flotation technique.

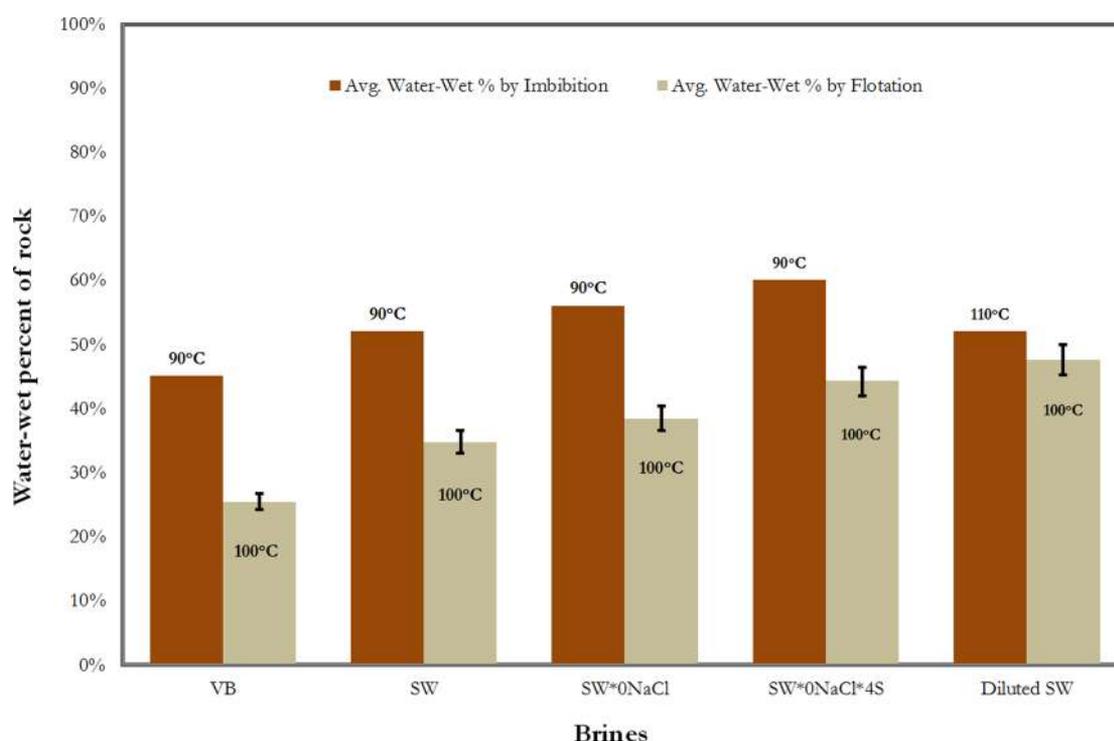


Figure 4. Comparison of imbibition and flotation water-wet percent of chinks. Imbibition water-wet percent of chalk was measured by running a chromatographic separation test.²⁸ Error bars represent $\pm 5\%$, the experimental uncertainty associated with the flotation technique.

Yousef et al.¹¹ recovered additional oil with diluted versions of seawater in Middle Eastern carbonate reservoir rock. The results for secondary recovery with dilution are shown in Figure 5 together with the wettability as determined by flotation. In the corefloods, the authors observed recovery increased with up to 20 \times dilution and then further dilution did not produce more. The flotation results show the increasing dilution made the system more water-wet up to 20 \times dilution, but greater dilution did not increase water-wetness. The agreement between recovery and change in wettability is good in spite of using different oil and reservoir mineralogy.

Fathi et al.²⁹ tested the effect of dilution on oil recovery using imbibition tests for Stevns Klint chalk. They found that oil

recovery increased with dilution. The oil recovery and wettability measured by flotation is plotted in Figure 6. The data show there is a connection between the additional oil recovery and wettability alteration to more water-wet conditions. The flotation data show that the increased recovery is somewhat associated with increasing water-wetness, but the correlation is not as strong as the coreflooding experiments.¹¹ For example, Figure 6 shows that the SW0NaCl*4S brine creates more water-wet conditions compared to SW0NaCl at the same operating conditions, but the SW0NaCl brine had better recovery. This may be due to the difference in conditions for the imbibition experiments that were conducted at lower temperature. The coreflood crude oil properties (AN = 0.25 mg

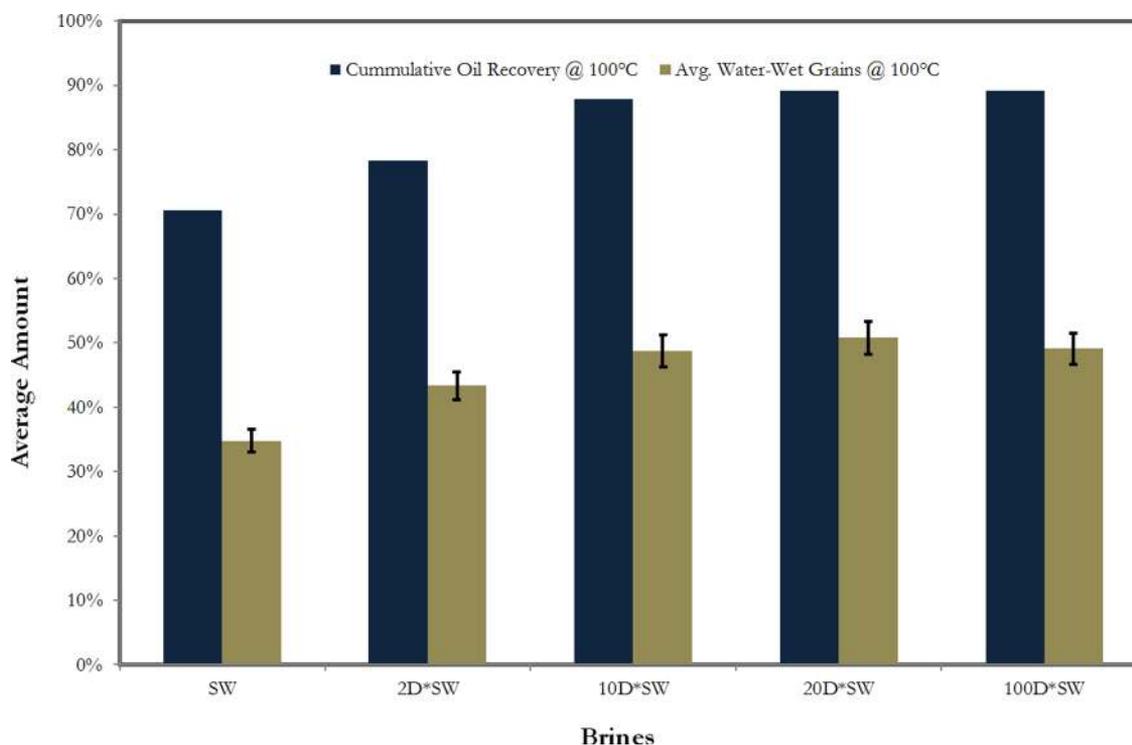


Figure 5. Comparison of additional oil recovery with wettability alteration as a result of diluted seawater injection in carbonate cores. Error bars represent $\pm 5\%$, the experimental uncertainty associated with the flotation technique.

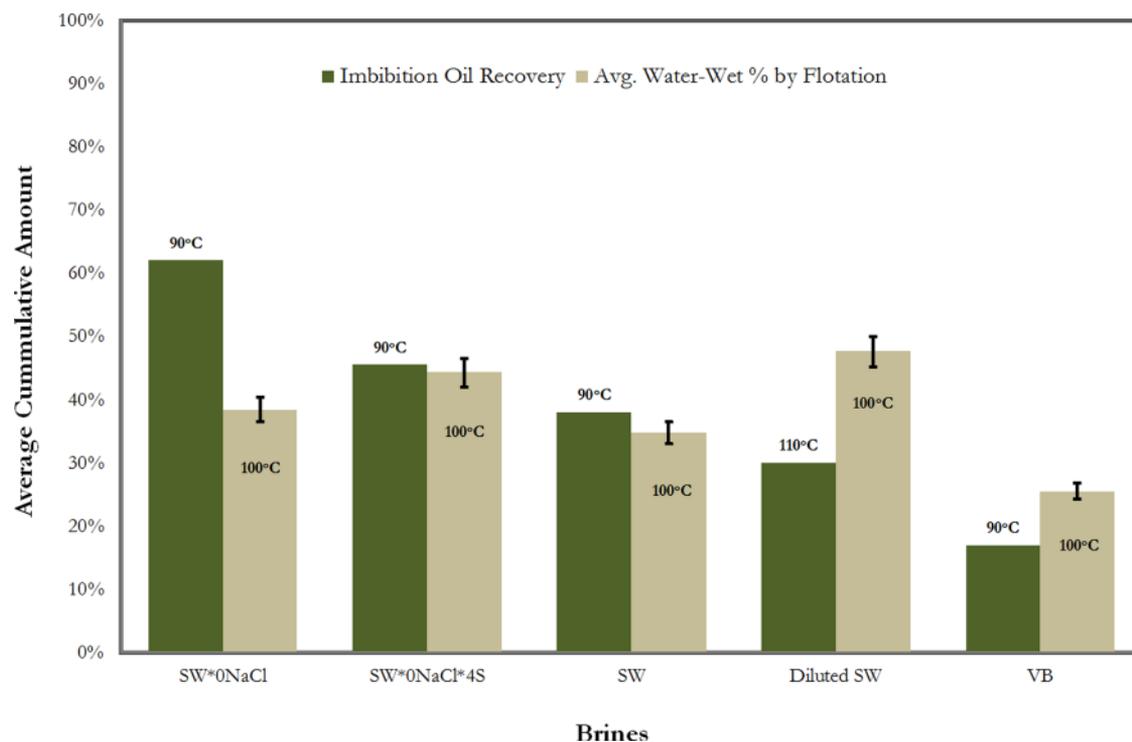


Figure 6. Comparison of additional oil recovery in chalk as a result of wettability alteration by imbibition and flotation experiments. Error bars represent $\pm 5\%$, the experimental uncertainty associated with the flotation technique.

of KOH/(g of oil)) and temperature (100 °C) were much more similar to the flotation experiments. However, the differences may reflect the fact that Fathi et al.²⁹ were testing the effect of sulfate in addition to dilution.

It is clear that there was no improved recovery due to dilution after approximately 10 \times , nor any change in wettability.

Therefore, it may be concluded that the degree of dilution that will improve water-wetting optimally is less than might be expected based on low salinity experiments, primarily in sandstones, that used 100 \times dilution. The optimum dilution factor can quickly and easily be identified by the flotation technique providing another advantage to the technique.

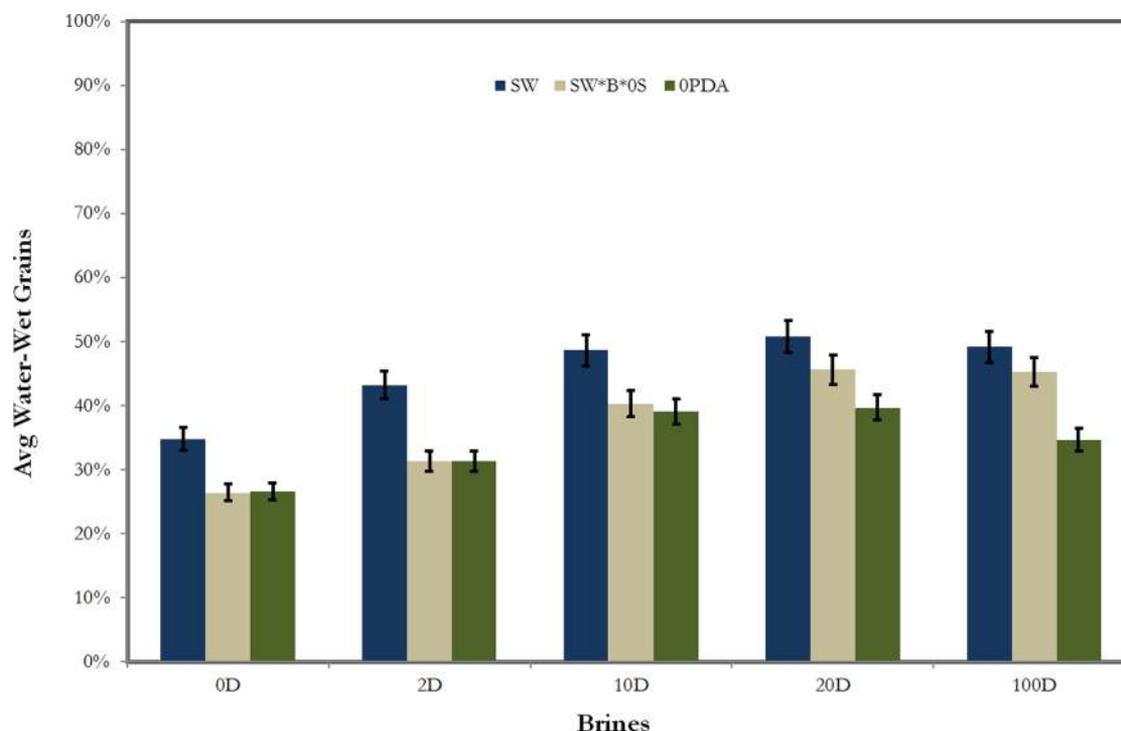


Figure 7. Comparison of wettability alteration caused by SW, SW*B*0S, and SW*0S. Error bars represent $\pm 5\%$, the experimental uncertainty associated with the flotation technique.

It is notable that the change in wettability toward water-wet condition in chalk measured by flotation followed the pattern of increased recovery in both chalk and limestone even though the crude-water-rock systems are different. So, while the degree of wettability alteration is not exactly the same as the amount of additional oil, the technique does indicate that the extra oil will be produced. The flotation experiments purely describe the wettability alteration potential of brine whereas in oil recovery processes the other factors as described above also contribute. Therefore, the total oil recovery is the combined effect of different processes, and flotation experiments allow us to better evaluate the contribution of wettability alteration in the total oil recovery.

3.3. Wettability and Potential Anions. It has been described by Sohal et al.¹⁹ that surface charge of carbonate minerals is slightly positive at reservoir conditions and usually depends on brine chemistry and pH. Therefore, the rock–brine interface is positively charged, while the oil–brine interface is negatively charged as a result of the carboxylic acids in oil. There have been several studies on the effect of potentially determining ions.^{9,29–34} PDI's are ions that can significantly change the surface charge of carbonates and include divalent Ca^{2+} , Mg^{2+} , and SO_4^{2-} . In their studies different concentrations and ratios of PDIs were used in synthetic seawater irrespective of whether precipitation issues were tested by coreflooding and imbibition experiments to improve the oil recovery. The improved recovery was often exclusively attributed to wettability alteration apart from other contributing factors.

In these studies the proposed mechanism was SO_4^{2-} adsorption on chalk surfaces that reduced the positive charge density of carbonate surface and allowed Ca^{2+} and Mg^{2+} to approach the surface to release carboxylic acid groups at temperature higher than 100 °C. In addition to sulfate, phosphate (PO_4^{3-}) and borate (BO_3^{3-}) have also been tested as potential anions to improve recovery in carbonates by Gupta

et al.¹⁰ But there is still a lack of systematic study that isolates the effect of low salinity (here low salinity is used as a relative term compared to formation water) and PDAs such as SO_4^{2-} and trivalent PO_4^{3-} and BO_3^{3-} to change the wettability. It becomes even harder to differentiate both effects using traditional coreflooding and imbibition methods when there is an internal source of potential anion (SO_4^{2-}) production such as anhydrite (CaSO_4).

The flotation technique can more easily differentiate the contribution of each type to improve water wetness as depicted in Figure 7. The synthetic seawater with sulfate, seawater with borate, and seawater without sulfate were used to observe the influence of PDAs and low salinity separately. Note that the concentration of borate (0.009 mol/L) is much lower compared to sulfate (0.024 mol/L) in seawater because borate produced precipitation at room temperature if higher concentrations were used.

Again using SW as the baseline, we observe that dilution increases water-wetness up to 10 \times dilution; then further dilution does not increase water-wetting. The SW*B*0S and SW*0S (0PDA) brines behave identically for SW and the 2 \times and 10 \times dilutions. However, the amount of wettability alteration is less for brines without sulfate with about 15% less water-wet grains compared to SW at the lower dilution factors. At dilution of 20 \times and 100 \times , borate is not as effective as sulfate but more effective than brine that lacks any PDA. The synthetic seawater used had 24 mmol/L sulfate versus 36 mmol/L borate in the borate-substituted seawater (Table 4). However, at the experimental pH values the dominant (>50%) aqueous species is the divalent anion, SO_4^{2-} , while the dominant aqueous species of boron is neutral H_3BO_3 (>90%) leaving only 5–10% as the borate anion. The effect of calcite surface charge from sulfate sorption can be described using eq 1, where $>\text{CaOH}_2^+$ is the positively charged surface site of calcite. The equation shows that the sulfate anion attaches to

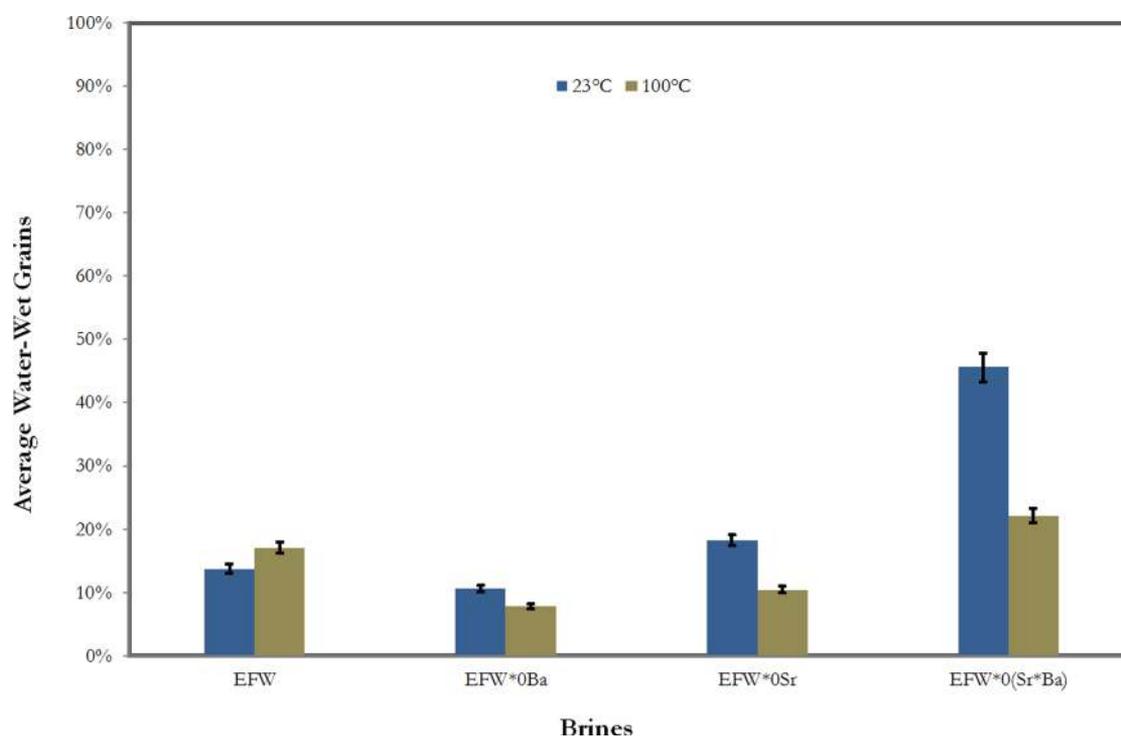


Figure 8. Effect of potential scale forming ions on wetting conditions. Error bars represent $\pm 5\%$, the experimental uncertainty associated with the flotation technique.

the positively charged site and renders the site negatively charged, shifting the overall surface charge. A similar equation could be written for borate, but the amount of borate available in solution is much less than the brine with sulfate. This is consistent with the observations of the smaller effect for borate.



The results suggest that borate can substitute for sulfate to some degree, but is probably limited in field applications by formation of precipitate and aqueous speciation at reservoir pH.

3.4. Wettability and Potential Scale Forming Ions. In formation brine every individual ion can play a vital role in wettability development. In flotation experiments we found that if chalk is aged with synthetic EFW with and without Sr^{2+} and Ba^{2+} ions, the initial wetting conditions are different. The EFW depleted in these ions produced 5% less oil-wet conditions compared to the EFW containing these potential scale forming ions at 100 °C as shown in Figure 8. These potential scale forming cations always remove from formation brine during the aging process to avoid the precipitation problems. But they significantly influence the initial wetting conditions. Suijkerbuijk et al.³⁵ also observed the same effect in sandstones and described that the depletion of potentially scale forming divalent cations, such as Sr^{2+} and Ba^{2+} , from artificial formation brines may lead to an unrepresentative wettability restoration (underestimating oil-wetness), because these ions are expected to play a disproportionately large role in the determination of the wettability state of a rock after aging, if the $\text{Mg}^{2+} \rightarrow \text{Ca}^{2+}$ trend is extrapolated. In most of the laboratory coreflood and imbibition experiments the core plugs were aged with synthetic formation water depleted in potential scale forming ions do have produce nonrepresentative wetting conditions. The data show that exclusion of these cations from brines will

overestimate water-wetness by as much as 35% at room temperature, although this is reduced to only 5% by 100 °C.

3.5. Retained Oil. The percent of oil-wet grains showed the extent of further wettability alteration potential for other more effective advanced fluids for the same rock crude system at given temperature. As it can be seen in Figure 4 SW*0NaCl*4S has more potential to improve water-wet conditions compared to SW*0NaCl at the same operating conditions.

The flotation technique provides data by direct observation of the adhesion of oil on water-wet grains, but also offers information about oil retained on the water-wet grains as shown in Figure 3. As described above, a portion of the water-wet grains become oil stained. The oil-staining is usually more prevalent on the top of the grain pile. Since the grains are fully agitated during the experiment, the oil must be entrained in the water-wet grains as it moves upward during phase separation. This oil offers additional information on the wettability alteration mechanisms compared to other wettability measurement techniques.

Consistent with our observations, Thomas et al.²⁷ observed that carbonate mineral surfaces were left with a visible brown color after exposure to organic compounds even if the surfaces remained water-wet. The authors observed that organic components of oil such as organic acids were strongly adsorbed (chemisorption) on carbonate surfaces, while other components such as alcohols and amines were weakly adsorbed (physisorped). The weakly sorbed species could be desorbed by most solvents, but strongly absorbed species could not. The adsorbed species altered the wettability as measured by contact angle. Long-chained organic acids in particular were strongly sorbed and formed monolayers on the mineral surface. In contrast, the sulfur-containing and nitrogen bases were weakly sorbed and the sorption was easily reversed.

The amount of oil attached to water-wet grains for SW and diluted SW is depicted in Figure 9. The amount of retained oil

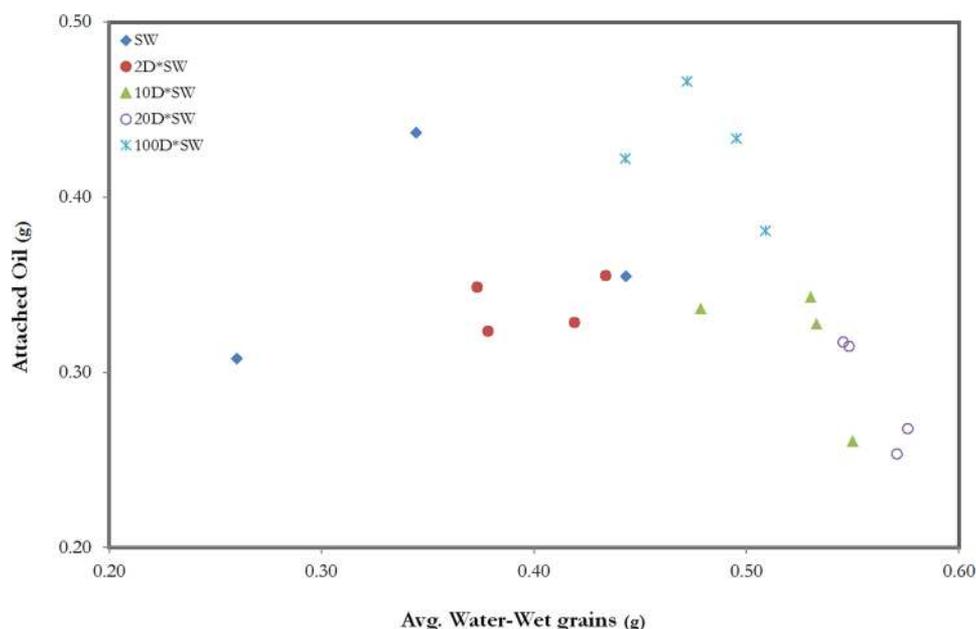


Figure 9. Oil adhesion on water-wet grains in the case of seawater and its different dilutions at 100 °C.

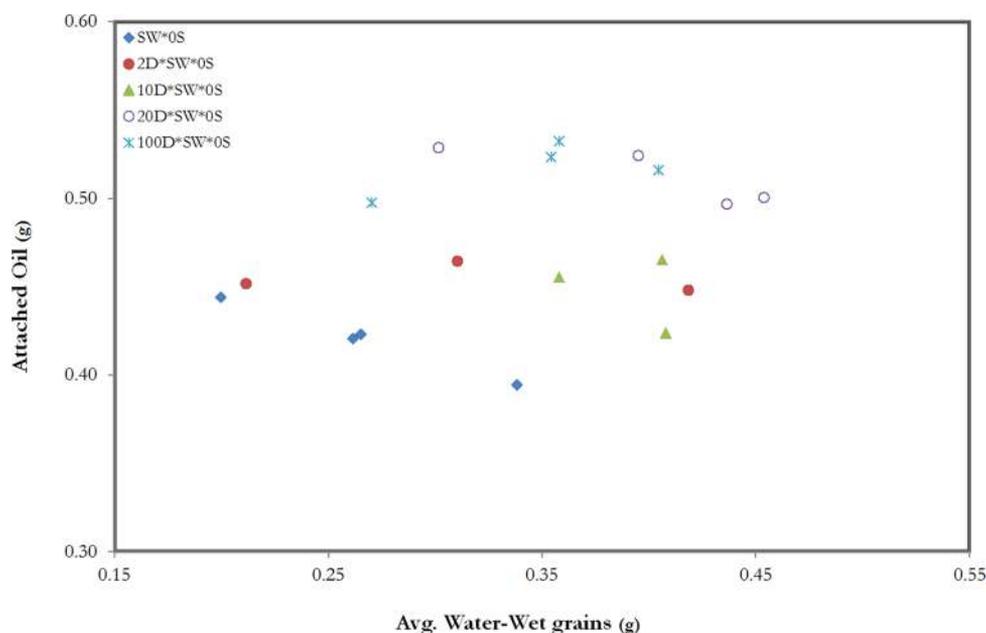


Figure 10. Oil adhesion on water-wet grains in the case of SW*0S for different dilutions at 100 °C.

is not correlated with the amount of water-wet grains, and the amount of refractory oil is similar at about 0.3 g for SW, 2D*SW, and 10D*SW. This suggests the adhesion is relatively insensitive to surface area. The 100-fold dilution shows the greatest amount of refractory oil and the 10-fold dilution the least. The 100-fold dilution shows the greatest amount of retained oil and the 20-fold dilution the least. The wettability of those solutions was the same within measurement error (Figure 5), so the sudden shift in retained oil does not appear to be due to a change in wettability.

The results for brines without sulfate are shown in Figure 10. The overall pattern is similar to seawater/diluted seawater with sulfate. The amount of retained oil is not correlated with grain mass. However, the amount of retained oil is significantly higher for all degrees of dilution. The SW*0S, 2D*SW*0S,

and 10D*SW*0S have similar amounts of retained oil, while the 20D*SW*0S and 100D*SW*0S solutions have higher amounts of retained oil. The absence of sulfate appears to enhance oil retention on the grain surfaces.

The results for seawater containing borate instead of sulfate (SW*B*0S) are shown in Figure 11. The pattern of data is similar to seawater with little correlation between grain mass and retained oil, but similar to seawater without sulfate in that more oil is retained on the water-wet grains compared to synthetic seawater. The borate brines show a trend of more retained oil as dilution increases with the maximum retained oil at 10× dilution. Further dilution did not increase retained oil, and again the amount of retained oil is not correlated with grain surface area. Since both sulfate and borate are oxyanions, we could expect them to have similar behavior with regard to

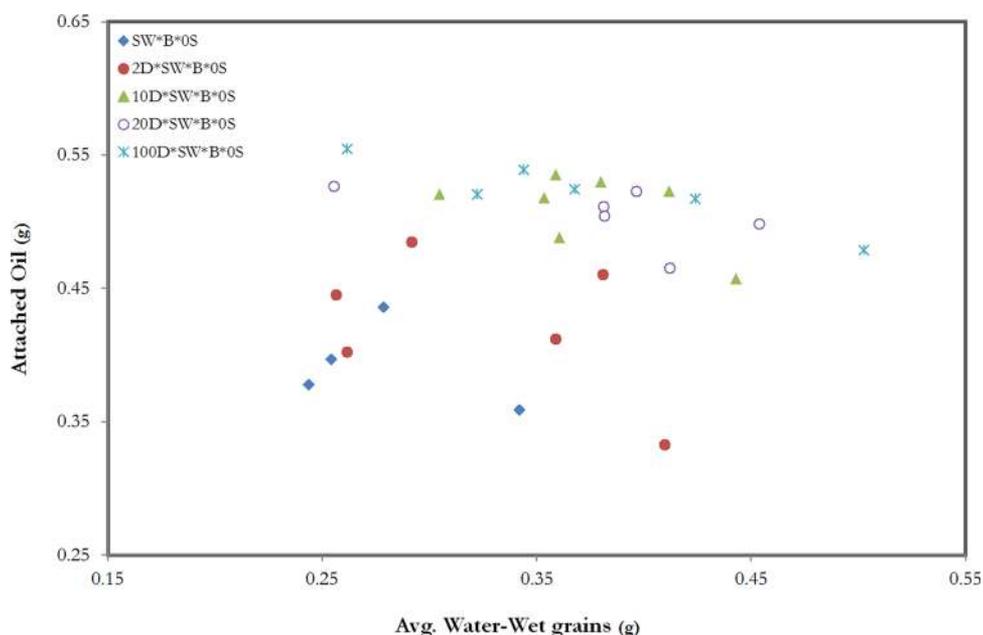


Figure 11. Oil adhesion on water-wet grains in the case of borate brines and diluted brines at 100 °C.

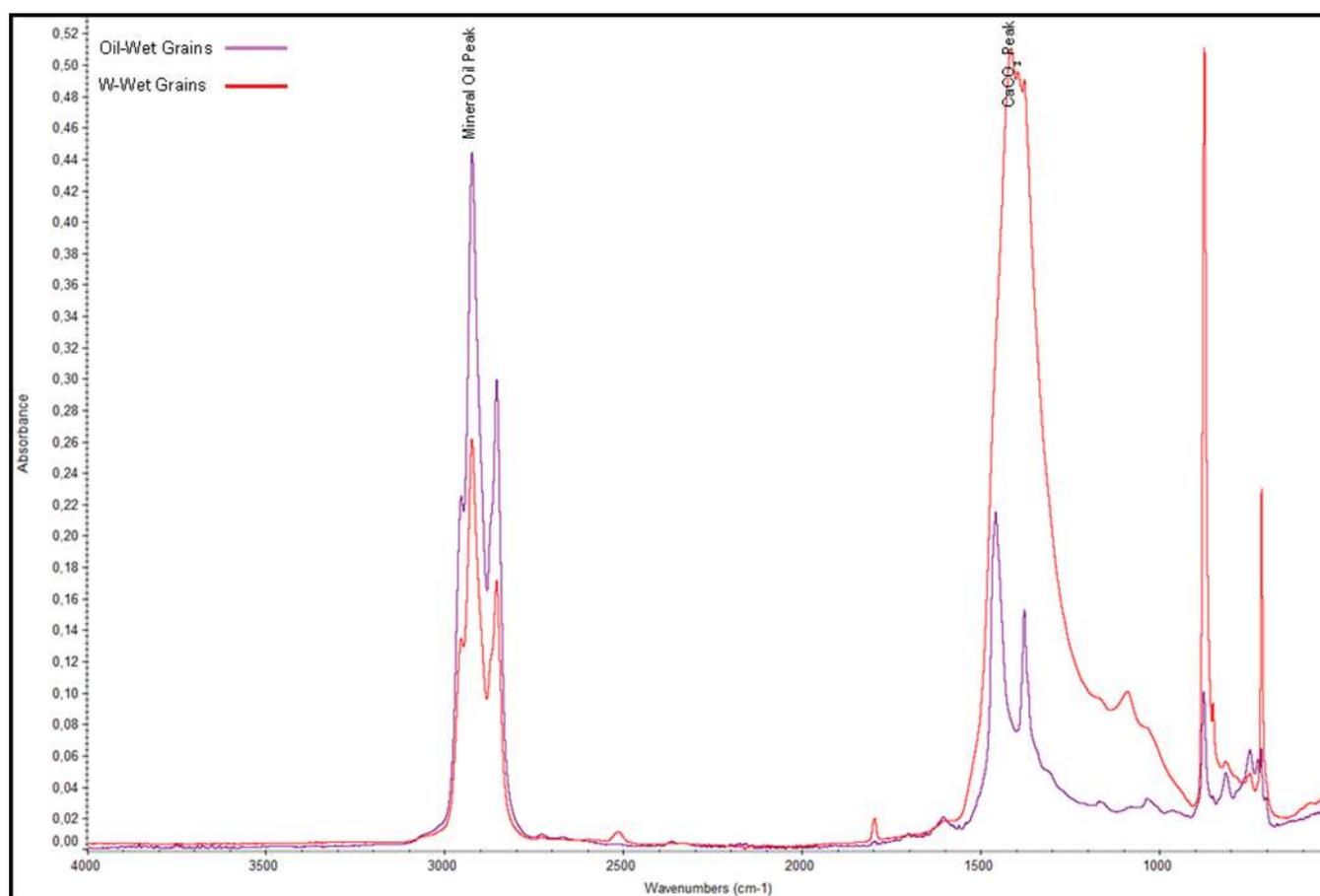


Figure 12. Amount of oil attached to water-wet and oil-wet grains.

wettability. Gupta et al.¹⁰ showed that substituting borate or phosphate for sulfate increased recovery compared to sulfate in limestone and dolomite cores without anhydrite. However, it appears that sulfate has a different effect than borate with regard to retained oil.

Infrared spectroscopy (IR spectroscopy) was used to measure the amount of oil bonded or attached to oil-wet and water-wet chalk grains. The oil coated water-wet and purely oil-wet chalk grains were dried at 45 °C for 24 h to remove water before putting them into the infrared spectrometer, iD7-ATR.

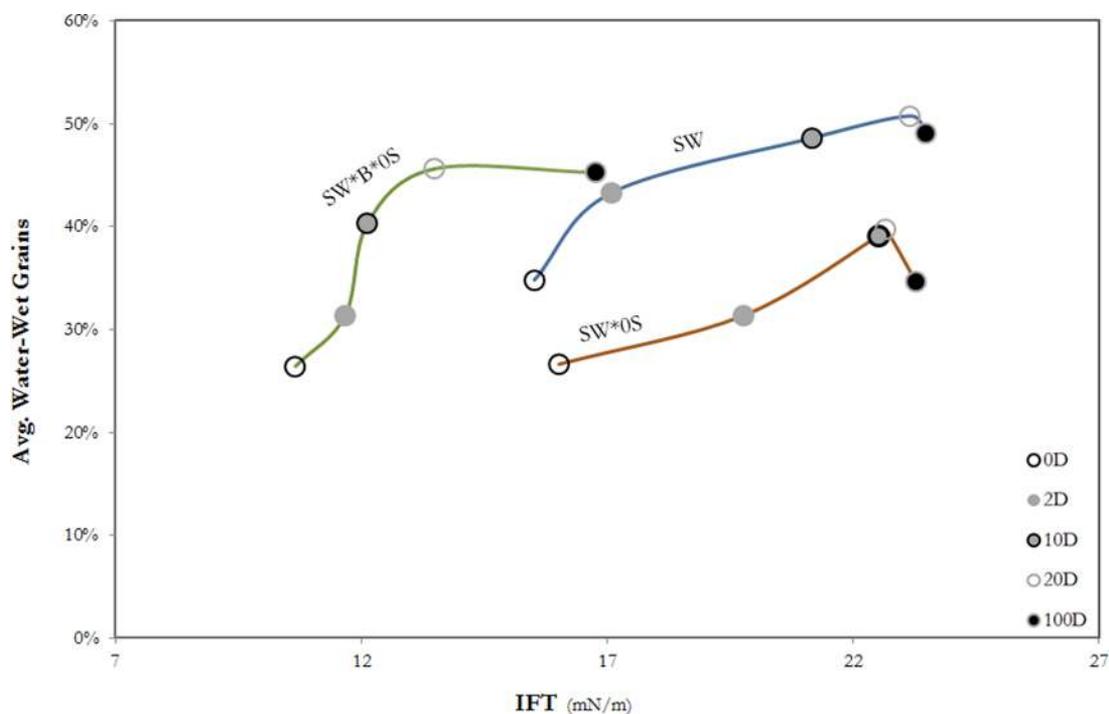


Figure 13. Correlation between IFT at 23 °C and average water-wet grains at 100 °C.

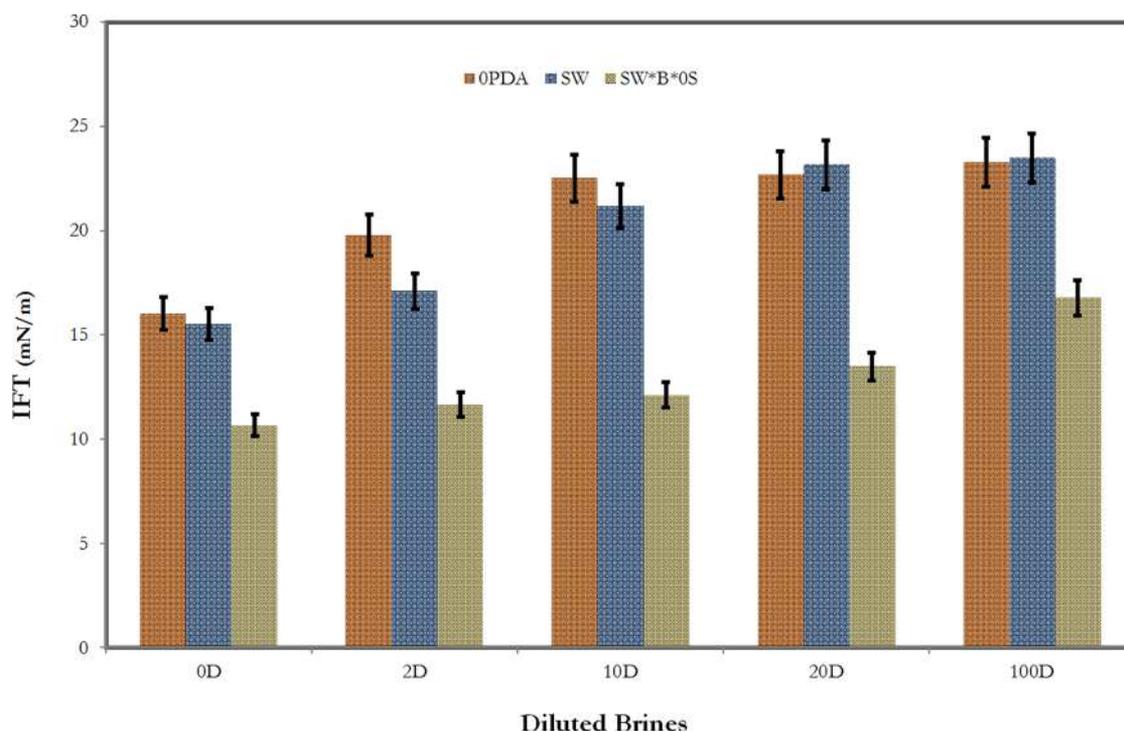


Figure 14. Relation between IFT and different brines with diluted versions at room temperature. Error bars represent $\pm 5\%$, the experimental uncertainty associated with the flotation technique.

In this technique a light with longer wavelength and lower frequency than visible light (infrared light) passed through the sample to induce vibrational excitation of covalently bonded atoms instead of electron excitation. So, molecules experience vibrational motions characteristics of their component atoms and absorb infrared radiation that corresponds in energy to these vibrations. The absorption spectra of compounds are a unique reflection of their molecular structure and thus used to

identify the substances. The generated IR spectrum is a graph of infrared light absorbance (transmittance) on vertical axis versus frequency or wavelength on the horizontal axis. Typical units of frequency used in IR spectra are reciprocal centimeters (cm^{-1}) instead of hertz (Hz) because the numbers are more manageable and also called wave numbers. This test was run to identify the amount of oil attached to oil-wet and oil coated water-wet chalk grains. It can be seen in Figure 12 the oil layer

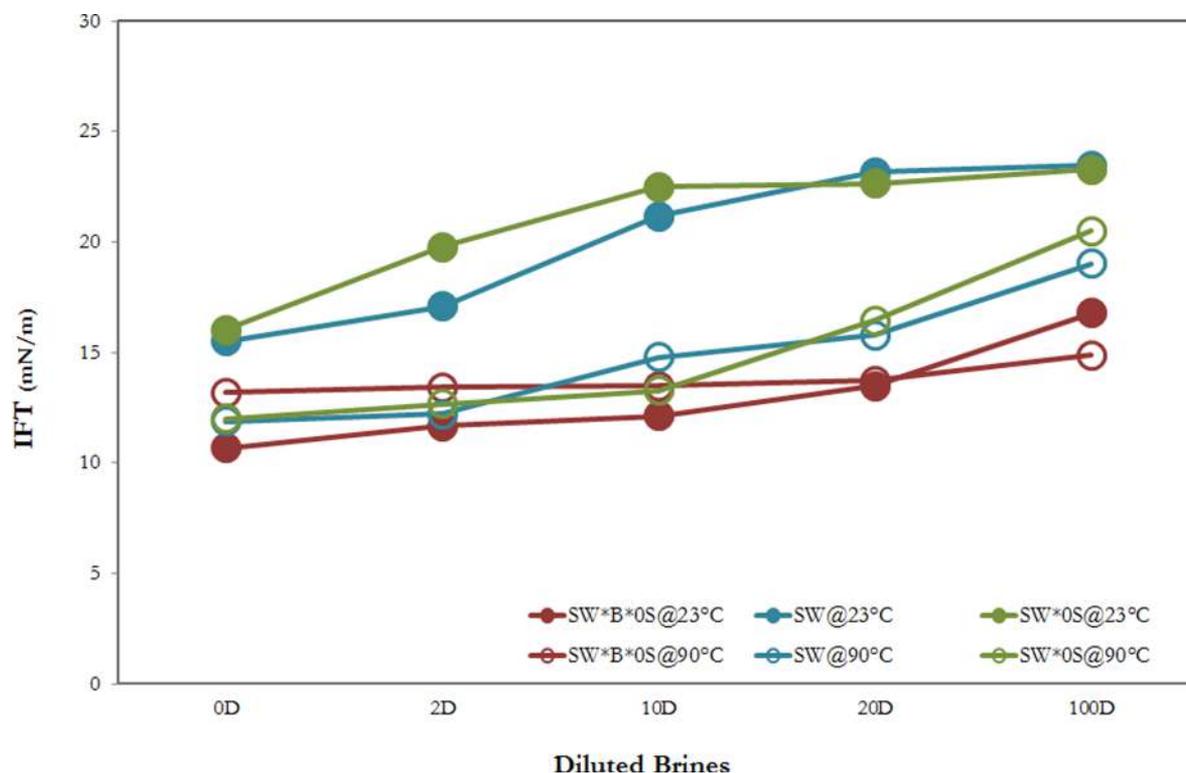


Figure 15. Effect of increasing temperature on IFT of diluted brines.

attached to oil-wet grains (peak at 2950 cm^{-1}) showing much higher absorbance (0.45) compared to water-wet grains an indication of a thicker oil layer. But the CaCO_3 peak at 1450 cm^{-1} (wave numbers) was much higher for water-wet grains compared to oil-wet grains. That means equipment detected the chalk through the thin oil layer at water-wet chalk grains while it could not be identified in the oil-wet case because the oil completely shielded the surface.

3.6. Wettability and IFT. The relative contribution of IFT and wettability to increase oil recovery is not well understood. Al-Attar et al.¹⁴ found no clear correlation between increased recovery and IFT for Abu Dhabi limestone/dolomite cores. Sheng³⁶ used the UTCHEM numerical model to match published experimental data and evaluate the sensitivity of recovery on each factor independently. He found that at high IFT values, wettability alteration is important, but that lowering IFT independently also increased recovery. Meng et al.³⁷ prepared synthetic seawater without SO_4^{2-} , Ca^{2+} , and Mg^{2+} to measure the contact angle and IFT. They used different concentrations of PO_4^{3-} in seawater and calculated minimum IFT values of 2.15 and 1.92 mN/m at 25 and 90 °C, respectively, for 1.0 g/L PO_4^{3-} . They found an increasing trend of IFT on diluting seawater. Figure 13 shows the effect of brine dilution on IFT for seawater (SW), seawater with borate (SW*B*OS), and seawater without any PDA's (OPDA's). We can see that dilution increased water-wetness and IFT values. There is a positive correlation between wettability alteration and increase in IFT. But the positive correlation between IFT and improvement in water-wet conditions only continue to 10X–20X dilution where the relationship inverted or remained constant.

Figure 14 shows that the brine with borate (SW*B*OS) decreased the IFT more than SW and SWOS. The value of IFT was temperature dependent with higher IFT values at 90 °C

compared to room temperature shown in Figure 15. But in many experimental studies^{12,38–40} the IFT had the opposite trend, decreasing IFT with dilution. Al-Attar et al.¹⁴ observed both trends of IFT change using different brines with the same crude oil at room temperature (25 °C). They also found an irregular pattern of IFT change based on a systematic increase of Ca^{2+} ion in brine. Since an IFT of 0.01 to 0.001 mN/m is required to improve the oil recovery by miscible displacement, alteration of IFT does not appear to be the principle mechanism to increase oil recovery due to the injection of low salinity water.

4. CONCLUSIONS

While there is no direct relationship between improved recovery and wettability alteration, many authors have linked increasing water-wetness to improved recovery. However, measurement of wettability is time-consuming and usually requires expensive equipment. Samples are limited to cores or mineral plates, and the scale is much greater than the grain surfaces where wettability alteration takes place. The flotation experiments can use core material or cuttings that are more readily available saving cores for traditional experiments. The technique measures wettability at the grain scale directly and is easy to use. Results for wettability are consistent with the published data for other chalk examples and showed the flotation technique can measure wettability reliably. The technique is fast and low cost and produces not just wettability measurements but also allows physical separation of oil-wet and water-wet surfaces for more in-depth study. Our results show that the technique could be used to determine the amount of dilution required to maximize wettability alteration in field application while minimizing costs associated with desalination.

Our results also show that wettability alteration toward more water-wet conditions was strongly correlated with dilution in chalk. These trends match those reported for calcite and dolomite. The shift in wettability toward more water-wet conditions reached the maximum effect at 10× dilution. Further dilution did not increase water-wetness. Experiments designed to separate dilution from the presence of potentially determining anions such as sulfate and borate showed PDA's enhance water-wetness for the same degree of dilution by 10–15%. We were also able to evaluate the roles of Sr^{2+} and Ba^{2+} in determining wettability and show their role in wettability can be significant and is temperature dependent. Brines without these common ions create a more water-wet condition than is likely to be present in the reservoir.

We were also able to quantify the amount of oil retained on the water-wet surfaces. Both water-wet and oil-wet surfaces retain strongly adsorbed components of the crude oil, but the coating is thicker on the oil-wet grains. The amount of strongly adsorbed oil was relatively insensitive to surface area but was dependent on water chemistry. The amount of oil attached to water-wet chalk grains was comparatively less than the amount bonded to purely oil-wet grains as identified in the IR spectrum.

The influence of IFT on wetting conditions was measured. A correlation between brine dilution and increasing IFT was quantified. While dilution for our experimental system did increase IFT, the trend does not favor better recovery nor is the magnitude of change sufficient to explain the increased recovery observed in laboratory or field cases.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sohal@bio.aau.dk.

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Sylte, J. E.; Hallenbeck, L. D.; Thomas, L. K. Ekofisk Formation Pilot Waterflood. *Proceedings of the SPE Annual Technical Conference and Exhibition*, Houston, TX, USA, Oct. 2–5, 1988; Society of Petroleum Engineers: Richardson, TX, USA, 1988; Paper SPE 18276, DOI: [10.2118/18276-MS](https://doi.org/10.2118/18276-MS).
- (2) Hallenbeck, L.; Sylte, J.; Ebbs, D.; Thomas, L. *SPE Form. Eval.* **1991**, *6*, 284–290.
- (3) Hiorth, A.; Cathles, L.; Madland, M. *Transp. Porous Media* **2010**, *85*, 1–21.
- (4) Brady, P. V.; Krumhansl, J. L.; Mariner, P. E. Surface complexation modeling for improved oil recovery. *Proceedings of the SPE Improved Oil Recovery Symposium*, Tulsa, OK, USA, Apr. 14–18, 2012; Society of Petroleum Engineers: Richardson, TX, USA, 2012; Paper SPE 153744, DOI: [10.2118/153744-MS](https://doi.org/10.2118/153744-MS).
- (5) Mahani, H.; Keya, A. L.; Berg, S.; Nasralla, R. The Effect of Salinity, Rock Type and pH on the Electrokinetics of Carbonate-Brine Interface and Surface Complexation Modeling. *Proceedings of the SPE Reservoir Characterisation and Simulation Conference and Exhibition*, Abu Dhabi, UAE, Sep. 14–16, 2015; Society of Petroleum Engineers: Richardson, TX, USA, 2015; Paper SPE 175568, DOI: [10.2118/175568-MS](https://doi.org/10.2118/175568-MS).
- (6) Austad, T.; Strand, S.; Høgenesen, E.; Zhang, P. Seawater as IOR fluid in fractured chalk. *Proceedings of the SPE International Symposium on Oilfield Chemistry*, Woodlands, TX, USA, Feb. 2–4, 2005; Society of Petroleum Engineers: Richardson, TX, USA, 2005; Paper SPE 93000, DOI: [10.2118/93000-MS](https://doi.org/10.2118/93000-MS).
- (7) Strand, S.; Standnes, D.; Austad, T. *J. Pet. Sci. Eng.* **2006**, *52*, 187–197.
- (8) Zhang, P.; Tweheyo, M. T.; Austad, T. *Energy Fuels* **2006**, *20*, 2056–2062.
- (9) Zhang, P.; Tweheyo, M. T.; Austad, T. *Colloids Surf., A* **2007**, *301*, 199–208.
- (10) Gupta, R.; Smith, G. G.; Hu, L.; Willingham, T.; Cascio, M. L.; Shyeh, J. J.; Harris, C. R. Enhanced waterflood for Middle East carbonate cores-impact of injection water composition. *Proceedings of the SPE Middle East Oil and Gas Show and Conference*, Manama, Bahrain, Sep. 25–28, 2011; Society of Petroleum Engineers: Richardson, TX, USA, 2011; Paper SPE 142668, DOI: [10.2118/142668-MS](https://doi.org/10.2118/142668-MS).
- (11) Yousef, A. A.; Al-Saleh, S.; Al-Kaabi, A. U.; Al-Jawfi, M. S. Laboratory investigation of novel oil recovery method for carbonate reservoirs. *Proceedings of the CSUG/SPE Canadian Unconventional Resources and International Petroleum Conference*, Calgary, Alberta, Canada, Oct. 19–21, 2010; Society of Petroleum Engineers: Richardson, TX, USA, 2010; Paper SPE 137634, DOI: [10.2118/137634-MS](https://doi.org/10.2118/137634-MS).
- (12) Al Harrasi, A.; Al-mamari, R. S.; Masalmeh, S. K. Laboratory investigation of low salinity waterflooding for carbonate reservoirs. *Proceedings of the SPE International Petroleum Conference and Exhibition*, Abu Dhabi, UAE, Nov. 11–14, 2012; Society of Petroleum Engineers: Richardson, TX, USA, 2012; Paper SPE 161468, DOI: [10.2118/161468-MS](https://doi.org/10.2118/161468-MS).
- (13) Zhang, Y.; Sarma, H. K. Improving Waterflood Recovery Efficiency in Carbonate Reservoirs through Salinity Variations and Ionic Exchanges: A Promising Low-Cost “Smart Waterflood” Approach. *Proceedings of the SPE International Petroleum Conference and Exhibition*, Abu Dhabi, UAE, Nov. 11–14, 2012; Society of Petroleum Engineers: Richardson, TX, USA, 2012; Paper SPE 161631, DOI: [10.2118/161631-MS](https://doi.org/10.2118/161631-MS).
- (14) Al-Attar, H. H.; Mahmoud, M. Y.; Zekri, A. Y.; Almehaideb, R.; Ghannam, M. *J. Pet. Explor. Prod. Technol.* **2013**, *3*, 139–149.
- (15) Alameri, W.; Teklu, T. W.; Graves, R. M.; Kazemi, H.; AlSumaiti, A. M. Wettability Alteration During Low-Salinity Waterflooding in Carbonate Reservoir Cores. *Proceedings of the SPE Asia Pacific Oil & Gas Conference and Exhibition*, Adelaide, Australia, Oct. 14–16, 2014; Society of Petroleum Engineers: Richardson, TX, USA, 2014; Paper SPE 171529, DOI: [10.2118/171529-MS](https://doi.org/10.2118/171529-MS).
- (16) Al-Shalabi, E. W.; Sepehrnoori, K.; Delshad, M. Mechanisms behind low salinity water flooding in carbonate reservoirs. *Proceedings of the SPE Western Regional & AAPG Pacific Section Meeting 2013 Joint Technical Conference*, Monterey, CA, USA, Apr. 19–25, 2013; Society of Petroleum Engineers: Richardson, TX, USA, 2013; Paper SPE 165339, DOI: [10.2118/165339-MS](https://doi.org/10.2118/165339-MS).
- (17) Al-Shalabi, E. W.; Delshad, M.; Sepehrnoori, K. Does the Double Layer Expansion Mechanism Contribute to the LSWI Effect on Hydrocarbon Recovery from Carbonate Rocks?. *Proceedings of the SPE Reservoir Characterization and Simulation Conference and Exhibition*, Abu Dhabi, UAE, Sep. 16–18, 2013; Society of Petroleum Engineers: Richardson, TX, USA, 2013; Paper SPE 165974, DOI: [10.2118/165974-MS](https://doi.org/10.2118/165974-MS).
- (18) Mahani, H.; Keya, A. L.; Berg, S.; Bartels, W.-B.; Nasralla, R.; Rossen, W. R. *Energy Fuels* **2015**, *29*, 1352–1367.
- (19) Sohal, M. A.; Thyne, G.; Sogaard, E. G. *Energy Fuels* **2016**, *30*, 1904–1914.
- (20) Swinburne, J.; Rudorf, G. *Sci. Am.* **1906**, *61*, 25202–25204.
- (21) Wang, B.; Peng, Y. *Miner. Eng.* **2014**, *66–68*, 13–24.
- (22) Mohammadi-Jam, S.; Burnett, D. J.; Waters, K. E. *Miner. Eng.* **2014**, *66–68*, 112–118.
- (23) Dubey, S.; Doe, P. *SPE Reservoir Eng.* **1993**, *8*, 195–200.
- (24) Wu, Y.; Shuler, P. J.; Blanco, M.; Tang, Y.; Goddard, W. A. *SPE Journal* **2008**, *13*, 26–34.
- (25) Thyne, G.; Mwangi, P.; Rao, D. Extensive Experimental Wettability Study in Sandstone and Carbonate-Oil-Brine Systems: Part 1 Screening Tool Development. *Proceedings of the SCA International Symposium*, Napa Valley, CA, USA, Sep. 16–19, 2013; Society of Core Analysts: Fredericton, NB, Canada, 2013; Paper SCA2013-84.

(26) Fan, T.; Buckley, J. S. Acid number measurements revisited. *Proceedings of the SPE/DOE Symposium on Improved Oil Recovery*, Tulsa, OK, USA, Apr. 22–26, 2006; Society of Petroleum Engineers: Richardson, TX, USA, 2006; Paper SPE 99884, DOI: [10.2118/99884-MS](https://doi.org/10.2118/99884-MS).

(27) Thomas, M. M.; Clouse, J. A.; Longo, J. M. *Chem. Geol.* **1993**, *109*, 201–213.

(28) Fathi, J. Water-Based Enhanced Oil Recovery (EOR) in Carbonate Reservoirs. Ph.D. thesis, Department of Petroleum Engineering, University of Stavanger, Norway, 2012.

(29) Fathi, S. J.; Austad, T.; Strand, S. *Energy Fuels* **2011**, *25*, 5173–5179.

(30) Strand, S.; Høgenesen, E. J.; Austad, T. *Colloids Surf., A* **2006**, *275*, 1–10.

(31) Austad, T.; Strand, S.; Puntervold, T. Is wettability alteration of carbonates by seawater caused by rock dissolution. *Proceedings of the SCA International Symposium*, Noordwijk, Netherlands, Sep. 27–30, 2009; Society of Core Analysts: Fredericton, NB, Canada, 2009; Paper SCA 2009-43.

(32) Fathi, S. J.; Austad, T.; Strand, S. *Energy Fuels* **2010**, *24*, 2514–2519.

(33) Fathi, S. J.; Austad, T.; Strand, S. Water-Based Enhanced Oil Recovery (EOR) by “Smart Water” in Carbonate Reservoirs. *Proceedings of the SPE EOR Conference at Oil and Gas West Asia*, Muscat, Oman, Apr. 16–18, 2012; Society of Petroleum Engineers: Richardson, TX, USA, 2012; Paper SPE 154570, DOI: [10.2118/154570-MS](https://doi.org/10.2118/154570-MS).

(34) Romanuka, J.; Hofman, J.; Ligthelm, D. J.; Suijkerbuijk, B.; Marcelis, F.; Oedai, S.; Brussee, N.; van der Linde, H.; Aksulu, H.; Austad, T. Low salinity EOR in carbonates. *Proceedings of the SPE Improved Oil Recovery Symposium*, Tulsa, OK, USA, Apr. 14–18, 2012; Society of Petroleum Engineers: Richardson, TX, USA, 2012; Paper SPE 153869, DOI: [10.2118/153869-MS](https://doi.org/10.2118/153869-MS).

(35) Suijkerbuijk, B.; Hofman, J.; Ligthelm, D. J.; Romanuka, J.; Brussee, N.; van der Linde, H.; Marcelis, A. Fundamental investigations into wettability and low salinity flooding by parameter isolation. *Proceedings of the SPE Improved Oil Recovery Symposium*, Tulsa, OK, USA, Apr. 14–18, 2012; Society of Petroleum Engineers: Richardson, TX, USA, 2012; Paper SPE 154204, DOI: [10.2118/154204-MS](https://doi.org/10.2118/154204-MS).

(36) Sheng, J. J. *Asia-Pac. J. Chem. Eng.* **2013**, *8*, 154–161.

(37) Meng, W.; Haroun, M.; Sarma, H.; Adeoye, J.; Aras, P.; Punjabi, S.; Rahman, M.; Al Kobaisi, M. A Novel Approach of Using Phosphate-spiked Smart Brines to Alter Wettability in Mixed Oil-wet Carbonate Reservoirs. *Proceedings of the SPE International Petroleum Exhibition and Conference*, Abu Dhabi, UAE, Nov. 9–12, 2015; Society of Petroleum Engineers: Richardson, TX, USA, 2015; Paper SPE 177551, DOI: [10.2118/177551-MS](https://doi.org/10.2118/177551-MS).

(38) Okasha, T. M.; Alshaiwaish, A. Effect of brine salinity on interfacial tension in Arab-D carbonate reservoir, Saudi Arabia. *Proceedings of the SPE Middle East Oil and Gas Show and Conference*, Manama, Bahrain, Mar. 15–18, 2009; Society of Petroleum Engineers: Richardson, TX, USA, 2009; Paper SPE 119600, DOI: [10.2118/119600-MS](https://doi.org/10.2118/119600-MS).

(39) Yousef, A. A.; Al-Salehsalah, S. H.; Al-Jawfi, M. S. New Recovery Method for Carbonate Reservoirs through Tuning the Injection Water Salinity: SmartWater Flooding. *Proceedings of the SPE EUROPEC/EAGE Annual Conference and Exhibition*, Vienna, Austria, May 23–26, 2011; Society of Petroleum Engineers: Richardson, TX, USA, 2011; Paper SPE 143550, DOI: [10.2118/143550-MS](https://doi.org/10.2118/143550-MS).

(40) AlShaikh, M.; Mahadevan, J. Impact of brine composition on carbonate wettability: A sensitivity study. *Proceedings of the SPE Saudi Arabia Section Technical Symposium and Exhibition*, Al-Khobar, Saudi Arabia, Apr. 21–24, 2014; Society of Petroleum Engineers: Richardson, TX, USA, 2014; Paper SPE 172187, DOI: [10.2118/172187-MS](https://doi.org/10.2118/172187-MS).