

## Low-salinity flooding in a selected carbonate reservoir: experimental approach

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**Abstract** Low-salinity waterflooding has been used to improve oil recovery for many decades. Several theories regarding the mechanism of low-salinity flooding have been discussed in the literature including interfacial tension reduction, wettability alteration, change in pH value, emulsion formation, and clay migration. This work presents the results of flooding tests on selected carbonate core samples taken from Bu Hasa field in Abu Dhabi using sea water and two field injection waters, Um-Eradhuma (UER) at 197,357 ppm and Simsima at 243,155 ppm. These results were used to evaluate the effects of brine salinity and ionic composition on the possible interactions of limestone rock/brine/and oil system and to identify the oil recovery mechanism. The field injection waters were diluted to salinities of 5,000 and 1,000 ppm and the optimum salinity was determined and then modified by varying the sulfate and calcium ion concentrations. Wettability alteration was determined by contact angle measurements. Interfacial tension measurements of the studied systems were also performed in an attempt to evaluate the flow mechanism with low-salinity flooding. The experimental results revealed that a significant improvement in the oil recovery can be achieved through alteration of the injection water salinity. Reducing the salinity of UER water from 197,357 to 5,000 ppm resulted in an improvement of oil recovery from 63 to 84.5 % of OOIP and the latter salinity was used to evaluate the impact of changing the sulfate and calcium ion concentrations on oil recovery. Results also indicated that sulfate

concentration has a significant effect on the flooding process and that increasing the sulfate concentration beyond some optimum concentration of 46.8 ppm resulted in a negative effect on the flooding process. Contact angle measurements indicated that lowering the solution salinity could shift the wettability of the system towards intermediate wettability levels and that the UER water exhibits higher shift toward intermediate wettability compared to other waters. Results also indicated that there is no clear correlation between the improvements in oil recovery and interfacial tension and the pH of the studied systems. The results of this work are useful for people working in this field.

**Keywords** Low-salinity flooding · IFT · EOR · Wettability · Oil recovery

### Introduction

Low-salinity waterflooding was first attempted by researchers at The University of Wyoming during the 90s by examining the effect of brine, crude oil, mineralogy and experimental procedure on rock surface-wettability. In the subsequent decade, the technology of low-salinity flooding was repeatedly implemented in the laboratory and in the field. Over the past decade low-salinity waterflooding has emerged as a viable enhanced oil recovery (EOR) method. Both laboratory tests and field trials have shown that injecting chemically modified water instead of seawater can lead to incremental oil recoveries. Although much research has been conducted, the governing physical and chemical mechanisms for this increase in recovery are not yet agreed upon, but are generally believed to involve some form of interaction between the rock, oil, and brine leading to changes in wettability, oil/water interfacial tension, or both.

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Yildiz and Morrow (1996) conducted core floods using Berea sandstone, Moutray crude oil and either sodium-based brine composed of 4 % NaCl + 0.5 % CaCl<sub>2</sub> or calcium-based brine composed of 2 % CaCl<sub>2</sub>. Recovery was higher with the calcium brine when the connate and injected brines were identical. The highest recovery was achieved by initially saturating the core with calcium brine, injecting Na brine until residual oil saturation was achieved, then injecting calcium brine. Tang and Morrow (1997) investigated the effects of connate and injection brine salinity, aging time and temperature on water flooding and imbibition with 3 different crude oils and 3 different brines. They concluded that in water floods with constant connate brine salinity and variable injected brine salinity, diluting injected brine 100 times produced ~5 % incremental oil recovery. In water floods with variable connate brine salinity and constant injected brine salinity, decreasing connate brine salinity dramatically improved recovery—about 40 % incremental oil recovery was achieved by diluted the connate brine 100 times.

Based on the above findings, researchers began to focus on the only variable that can be manipulated in a reservoir—the injection brine salinity. Researchers noticed that improved recovery by injection of low-salinity brine only occurred when crude oil and clay bearing sandstone mineralogy were present. Based on this observation, Tang and Morrow (1999a, b) offered the first theoretical interpretation of the mechanism responsible for the recovery improvement. They observed an increase in water flood and spontaneous imbibition recovery with a decrease in salinity in numerous cases. The authors used Berea cores, CS crude, and refined oil and 7 different brines ranging from 35,960 ppm TDS down to 151.5 ppm TDS. Oil Recovery improved significantly in the CS reservoir and Berea cores when low-salinity brine was injected instead of high salinity, but recovery improved only marginally in the more clay-free cores. Berea cores that were fired and acidized, to stabilize fines, were insensitive to brine salinity. Tang and Morrow (1999a, b) concluded that heavy polar components in the crude oil adsorb onto fine particles along the pore walls and that these mixed-wet fines are stripped by low-salinity brine, altering wettability and increase oil recovery.

Zhang and Morrow (2006) conducted water flood and spontaneous imbibition experiments using 4 different samples of Berea sandstone and three different crude oils. These authors observed improved recovery by injecting low-salinity brine in secondary and tertiary modes. The impact of low-salinity brine varied significantly between the different samples of Berea, suggesting that mineralogy was the most important variable affecting improved recovery. The lowest permeability block of Berea ( $k_{\text{nitrogen}} \sim 60\text{--}140$  md) showed no sensitivity to salinity. The lack

of response was attributed to the presence of chlorite. In several cases, cores responded to low-salinity brine in the secondary but not the tertiary mode. Low-salinity effects become more dramatic as the initial water saturation increased. In all cases, injection of low-salinity brine was accompanied by an increase of pressure followed by a gradual decrease. Effluent pH also increased.

Some publications indicated that there is no benefit of low-salinity waterflooding. Sharma and Filoco (2005) investigated the impact of connate and injection brine salinity and crude oil on oil recovery, residual saturations and wettability using Berea cores, 3 different oils and NaCl brine in various concentrations. In their imbibition experiments, decreasing connate water salinity increased recovery and significantly affected relative permeability. The salinity of the displacing brine had no significant impact. Drainage experiment's recovery and relative permeability were insensitive to salinity. During waterflooding of crude oil, oil recovery increased with decreasing connate brine salinity. However, during waterflooding of mineral oil, recovery was insensitive to connate brine salinity. In all cases, waterflood recovery was insensitive to the salinity of the injected brine. Sharma and Filoco suggested that low-salinity connate brine changes the wetting properties of the rock surface from water-wet to mixed-wet and thereby increase the recovery.

Webb et al. (2003) observed a reduction in residual oil saturation in the near wellbore region by injecting low-salinity brine. Three different brines were injected into a clastic formation from a producing well. Saturation was measured after each injection using a pulsed neutron capture log. A base line  $S_{\text{or}}$  was established with a synthetic native brine (250,000 ppm). Synthetic sea water (120,000 ppm), injected second, did not reduce oil saturation further. Low-salinity brine (3,000 ppm), injected last, reduced  $S_{\text{or}}$  significantly in two sand intervals and slightly in another.

Zhang et al. (2007) reported increased recovery in the tertiary mode by reducing reservoir brine salinity 20 times. Two consolidated reservoir sandstone cores were used. X-ray diffraction indicated that each of the cores were rich in chert and kaolinite. Two different crudes and a mineral oil were used. Almost 70 % incremental oil recovery was achieved in the secondary mode. Both the high and low-salinity secondary floods were conducted in the same core. Tertiary recovery was also quite large; 25 % incremental recovery in the best case. The recovery was achieved slowly, taking more than 10 injected pore volumes. In several cases, the pH fell upon injection of low-salinity brine; contrary to other researcher's observations. Pressure drop was closely tied to incremental recovery. In all cases, where significant incremental recovery was achieved pressure drop increased significantly then fell gradually.

Pu et al. (2008) observed low-salinity tertiary recovery from an almost clay-free core for the first time. They injected coalbed methane (CBM) water into 3 sandstone reservoir cores composed of quartz, feldspar, dolomite, and anhydrite cements but which had very little clay. The CBM water's salinity was about 1,316 ppm TDS. Cores were first waterflooded with high salinity formation brine (38,651 ppm). When oil production due to high salinity brine ceased CBM water was injected. In all cases CBM water liberated additional oil. In each core, the benefit of tertiary low-salinity flooding became less dramatic after each flood and restoration. A core was acidized to remove dolomite crystals and subsequently its recovery became insensitive to low-salinity flooding. Pu et al. proposed that dolomite crystals play an important role in the low-salinity recovery mechanism. Some of the dolomite crystals become mixed-wet as they contacted the oil phase during aging. During the low-salinity flood the dolomite crystals may detach from the pore walls releasing oil from the rock surface. The detached dolomite crystals will then reside at the crude oil/brine interface increasing resistance to flow of brine at the interface, delay snap-off at pore-throats and preventing the collapse of oil lamella.

Bagci et al. (2001) studied the effect of brine composition on oil recovery by water flooding using limestone cores. Ten different brine compositions were examined for injection through the study. The brines were NaCl, CaCl<sub>2</sub>, KCl, and binary mixtures of them at two different concentrations (2 and 5 wt%). The highest oil recovery was 35.5 % of original oil in place (OOIP) for 2 wt% KCl. The authors concluded that any adjustment to the injected brine composition of a mature waterflood can offer a possible and economically feasible approach to increase oil production. Wettability alteration was mentioned as a reason for recovering more oil but without any further explanation. These authors used long core samples (20 inches) in the flooding experiments and at a reservoir temperature of 122 °F. Low-salinity effluent brine samples showed higher pH and that was caused by ions exchange reaction.

Høgenesen et al. (2005) concluded that any modification to the injection water ions can impact rock wettability and that can result in additional oil to be recovered. They presented an imbibition study at high temperature condition using reservoir limestone, outcrop chalk cores, seawater and formation water. The results showed that increasing the sulfate ion concentration at high temperature can act as a wettability modifying agent in carbonates, and increased the oil recovery. Scale and souring problems will be enhanced as increasing the sulfate concentration in the injected water. Moreover, this strategy has limitations with regard to initial brine salinity and temperature. At low temperature condition, cationic surfactant was mixed with

the aqueous solution and that increased the spontaneous imbibition through the cores.

Webb et al. (2005) presented a study that compared oil recovery from a North Sea carbonate core samples using sulfate-free formation simulated brine, with seawater, which contains sulfate. The imbibition capillary pressure experiments were performed at reservoir conditions using live crude oil and brine. The final results showed that the simulated seawater was able to modify the wettability of the carbonate system, changing the wettability of the rock to a more water-wet state. This conclusion was based on the saturation change noted in the spontaneous imbibition tests between simulated formation water and sea water.

Most of the low-salinity waterflood studies were conducted on limestone; seawater, also, was recommended as an injection fluid in chalk formations. Strand and Austad (2008) explained in preliminary experimental studies the chemical mechanism for the wettability alteration in fractured limestone after injecting seawater, sodium chloride brine, and formation water.

Synthetic seawater with and without sulfate ions was used to determine the sulfate ions effect on wettability. Spontaneous imbibition results at 248 °F showed 15 % increase in the oil recovery when limestone core was imbibed with seawater compared to seawater free of sulfate ions. Seawater has the lowest TDS compared to the other examined brines, but it did not include any brine test that has lower salinity than seawater. More details on reaction mechanism will be explained in the next section. Fjelde (2008) presented results on low-salinity water that increased oil recovery in limestone formation. Spontaneous imbibition experiments were conducted using formation water and low-salinity water. Low-salinity water showed similar oil recovery results to seawater experiments. No further details were mentioned in this work. Paul Vledder et al. (2010) work showed that the wettability can be changed at a reservoir scale, similar to more controlled experiments such as laboratory experiments and Log-Inject-Log tests. A large number of observations consistently prove this change in wettability that is shown to lead to an increased recovery factor. The incremental recovery due to the change in wettability on a field wide scale is 5–15 %. This range mostly overlaps with the range obtained from the experimental data (9–23 %) and therefore the final conclusion is that the incremental recovery due to low-salinity injection in Omar Field amounts to 10–15 % of the STOIP. The main issues to be managed are water sourcing, water disposal and water mixing in the reservoir.

The objective of this work is to investigate the merits of using low-salinity flooding techniques to enhance oil recovery in Bu Hasa reservoir, identify the mechanism involved in the additional recovery of oil by low-salinity

flooding, and evaluate the effect of different ions ( $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ ) on the overall recovery process.

## Experimental materials and setup

### Materials

Reservoir crude oil from Bu Hasa field was used in all experiments. The oil was filtered through a 5.0- $\mu\text{m}$  filter paper (with a vacuum pump) to remove any possible solid particles. The oil is sweet oil and has no  $\text{H}_2\text{S}$  and about 2.6 mole%  $\text{CO}_2$  which is very low. The oil density and viscosity are 0.825 g/cc and 3.08 cp measured at room temperature of 25 °C, respectively. Four types of water were used. The first type was Um-Eradhuma (UER) water which is the injection water that has been used in flooding the reservoir for many years. A live sample of this water was filtered, degassed, and then used in the experiments. This water has a salinity of 197,357 ppm and density of 1.15 g/cc. The second type was Simsima (SIM) water which is formation water that has been used in water flooding the reservoir for many years. A live sample of this water was filtered, degassed, and then used in the experiments. Its salinity is 243,155 ppm and its density is 1.16 g/cc. The third type is sea water (SW) which was collected from one of the Arabian Gulf beaches in Abu Dhabi. It was filtered, degassed, and then used in the experiments. Its salinity is about 40,980 ppm and its density is 1.029 g/cc. The fourth type was lab-prepared distilled water. Table 1 shows the analysis of these water samples.

Five core samples were selected from well number 589 in Bu Hasa field. The physical properties of these cores are listed in Table 2. Four of these core samples were used in the flooding experiments, namely, numbers 31, 39, 40, and 42. The fifth core sample (no. 46) was used for contact angle measurements. The mineral composition of these core samples and others are listed in Table 3.

### Experimental setup

Oil floods were conducted at constant injection pressure of 689.476 kPa (100 psi) with overburden pressure of 5,515.808 kPa (800 psi) and at room temperature of 25 °C (77 °F). The cores were positioned in a vertical

configuration and oil was injected at the top as illustrated in Fig. 1. Effluent rate was regularly measured with a stop watch and pressure drop was monitored continuously. The core holder was designed for high pressure flood tests and to accommodate core samples of 3.86 cm (1.52 in.) in diameter and a maximum of 7.62 cm (3 in.) in length.

The core samples were first saturated with formation water and displaced by crude oil to  $S_{wc}$  using the standard Core Lab procedures. The analysis of this water is presented in Table 4. The crude oil-saturated cores were then aged in crude oil for 4 weeks and then flooded with various brines. The volumes of produced brine and oil were recorded as a function of time at constant pressure drop. To avoid fingering of the displacing phase, these flooding processes were conducted at low rate between 1 and 3 cc/min. The injection of brine continued until oil ceased to show any production at the core outlet. The measured stable pressure drop(s) and the corresponding flow rate(s) were used to calculate end-point water permeability to water  $(k_{rw})_{Sor}$  using Darcy's law. For example, the values of  $(k_{rw})_{Sor}$  when flooding oil with 5,000 ppm UER water and 171,585 ppm UER water are 0.17 and 0.29, respectively. This observation is indicative of the system's wettability shift toward more water-wet as the end-point relative permeability to water decreases with decreasing of UER water salinity.

The material balance was then applied to calculate the residual oil saturation ( $S_{or}$ ). Figure 2 illustrates a block diagram of all test runs performed in this work. Experiments were conducted with UER water, SIM water, SW and distilled water. Experiments were then conducted using the dilutions of each type of water to determine the optimum water salinity. The effect of ionic concentration of sulfate and calcium ions on the flooding process was investigated using the optimum water salinity.

## Results and discussion

### Flooding with UER water

In order to evaluate the effect of different salinities on the recovery eleven core flooding tests were conducted. The UER brine was diluted to one-half of its original salinity, i.e., down to 98,679 ppm then to 5,000 ppm and finally to

**Table 1** Analysis of the different types of water

Type	mg/L								TDS (ppm)
	$\text{Ca}^{++}$	K	$\text{Mg}^{++}$	$\text{Na}^+$	$\text{CO}_3$	$\text{HCO}_3^-$	$\text{Cl}^-$	$\text{SO}_4^-$	
SIM	20,808	–	3,047	68,214	–	119	150,617	350	243,155
UER	14,033	–	3,024	57,613	–	244	122,023	420	197,357
SW	600	–	1,560	13,900	–	200	24,300	420	40,980

**Table 2** Properties of the selected core samples

Sample no.	Depth (m)	L (cm)	D (cm)	kw (md)	Dry weight (g)	Saturated weight (g)	Pore volume (cc)	$\phi$ Fraction
31	2650.206	7.090	3.843	8.7	164.080	186.700	20.423	0.248
39	2650.267	7.032	3.850	8.5	163.470	184.960	19.402	0.237
40	2650.937	7.247	3.853	8.7	170.210	192.370	20.007	0.237
42	2652.309	7.272	3.855	8.8	190.160	205.030	13.425	0.158
46	2652.400	7.160	3.860	7.7	190.800	204.130	12.035	0.144

**Table 3** X-ray diffractograms mineral composition of core samples

Sample no.	Major mineral	Minor mineral
31	Calcite (CaCO <sub>3</sub> )	Dolomite [CaMg(CO <sub>3</sub> ) <sub>2</sub> ]
39	Calcite (CaCO <sub>3</sub> )	Dolomite [CaMg(CO <sub>3</sub> ) <sub>2</sub> ]
40	Calcite (CaCO <sub>3</sub> )	Dolomite [CaMg(CO <sub>3</sub> ) <sub>2</sub> ]
42	Calcite (CaCO <sub>3</sub> )	Dolomite [CaMg(CO <sub>3</sub> ) <sub>2</sub> ]
46	Calcite (CaCO <sub>3</sub> )	Dolomite [CaMg(CO <sub>3</sub> ) <sub>2</sub> ]

1,000 ppm. The flooding results of this set of experiments are plotted as oil recovery percent of OOIP versus pore volumes injected of brine as shown in Fig. 3.

Figure 3 shows that the highest oil recovery was obtained from the 5,000 ppm dilution which is about 84.5 % of the OOIP. The lowest oil recovery percent observed when using the distilled waters was about 60.5 % of the OOIP. The 1,000 ppm dilution yielded a lower oil recovery than the 5,000 ppm solution and all the diluted UER waters resulted in a higher oil recovery than the distilled water. Therefore, the salinity of 5,000 ppm was considered as the optimum salinity for further evaluation.

**Flooding with SIM water**

Simsima brine with its original salinity of 243,155 ppm was first diluted by 50 % (salinity of 121,578 ppm) then down to 5,000 ppm and finally to 1,000 ppm. The results of this part are illustrated in Fig. 4.

Figure 4 shows that the highest oil recovery of 74.4 % of the OOIP was obtained with the 1,000 ppm dilution. The lowest oil recovery of 48.9 % of the OOIP was observed with the original SIM water. The 50 % dilution resulted in a recovery percent of 53.5 % of the OOIP then the 5,000 ppm dilution resulted in a recovery of 70.0 % of the OOIP.

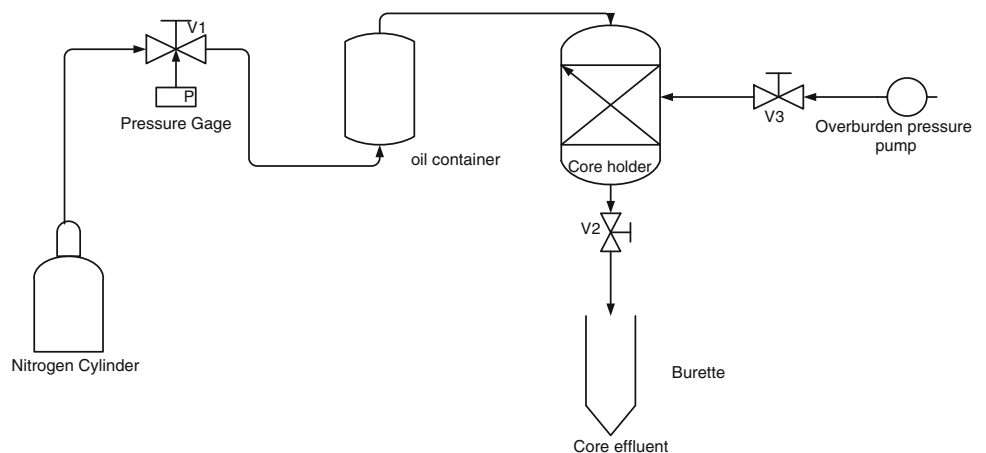
**Flooding with sea water**

Sea water brine of original salinity of 40,980 ppm was diluted to 5,000 ppm. The results of this section are shown in Fig. 5.

Figure 5 shows that original SW resulted in a recovery of 60.2 % of the OOIP and the 5,000 ppm brine showed a recovery of 62.2 % of the OOIP and the distilled water resulted in a recovery of 60.5 % of the OOIP. The three waters resulted in comparable results as there is no significant increase in oil recovery by dilution.

The results presented in Figs. 3, 4, and 5 show that flooding core samples with the three different brines at their original salinities resulted in the lowest ultimate oil recoveries. Also, by diluting these brines to lower salinities the oil recovery increased significantly except for SW as its original salinity is not high as in UER and SIM brines. The highest oil recovery of 84 % of OOIP recovery was achieved by flooding with UER brine at 5,000 ppm. Tang and Morrow (1999a, b) observed similar trends and

**Fig. 1** A schematic diagram of the core flooding setup



attributed these improvements to the presence of clay in their core samples. They concluded that the flow mechanism in low-salinity flooding is highly controlled by the clay. The core samples used in this work are clay-free and

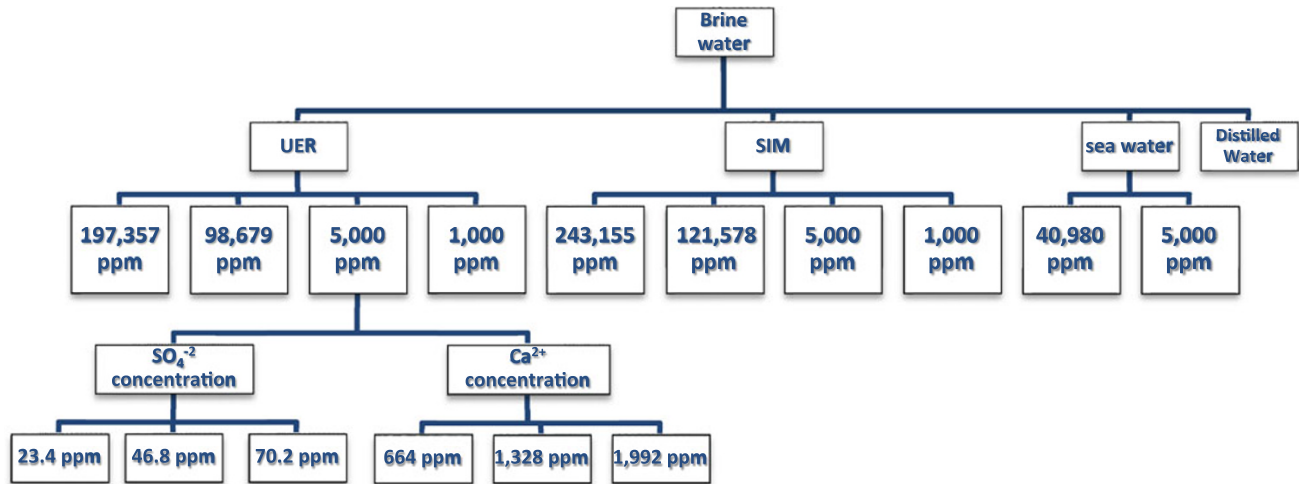
therefore another flow mechanism was responsible for the increased oil recovery by low-salinity flooding. Pu et al. (2008) observed increased oil recovery but in clay-free core samples. They proposed that dolomite crystals could play an important role in the low-salinity recovery mechanism.

**Table 4** Analysis of formation water

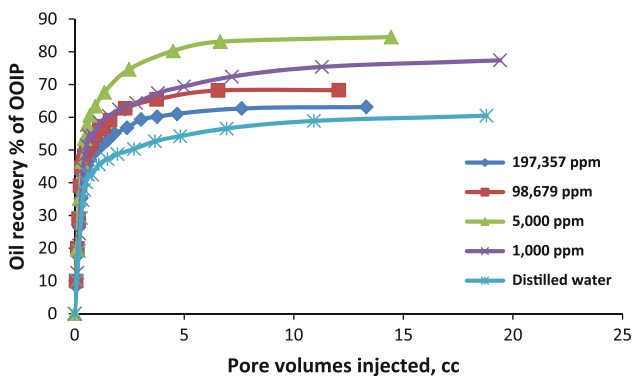
Element	Concentration, mg/L
Sodium	51,820
Calcium	15,992
Magnesium	1,282
Iron	277
Barium	0
Chloride	111,852
Bicarbonate	391
Sulfate	272
Carbonate	0
Hydroxide	0

Results of changing ionic composition of the brine

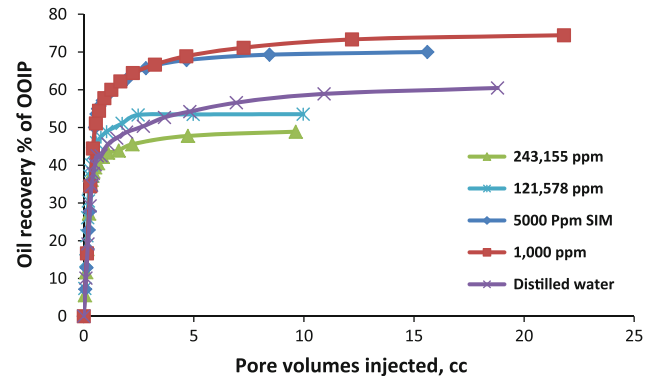
To evaluate the effect of  $Ca^{2+}$  and  $SO_4^{2-}$  concentrations on the performance of low-salinity flooding, two sets of core flooding runs were conducted. The 5,000-ppm dilution of UER brine was used as the base water for evaluating the effect of ionic composition because the highest oil recovery of 84 % of the OOIP was achieved by the 5,000-ppm dilution of UER brine. The first set of experiments involved flooding core samples with water UER at 5,000 ppm and sulfate concentrations of 11.7, 23.4, 46.8, and 70.2 ppm, respectively. Brine concentration was varied by changing



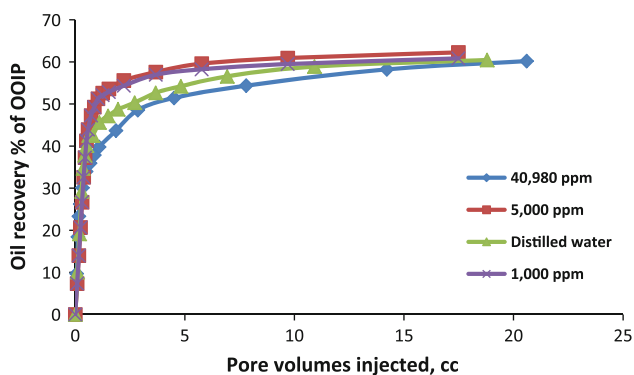
**Fig. 2** Block diagram showing the various experimental runs performed in this work



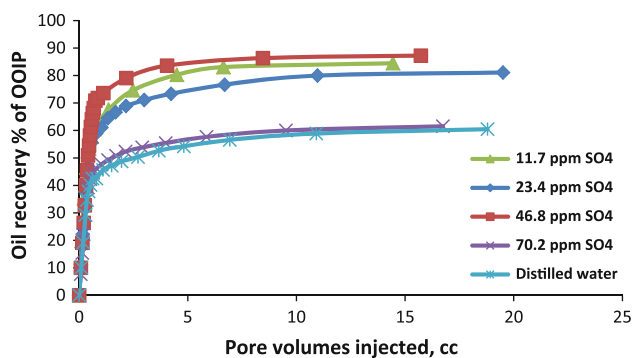
**Fig. 3** Oil recovery % of OOIP versus pore volumes injected of UER water with different salinity concentrations; figures between brackets represent percent of dilution of original salinity concentration



**Fig. 4** Oil recovery % of OOIP versus pore volumes injected of SIM water with different salinity concentrations; figures between brackets represent percent of dilution of original salinity concentration



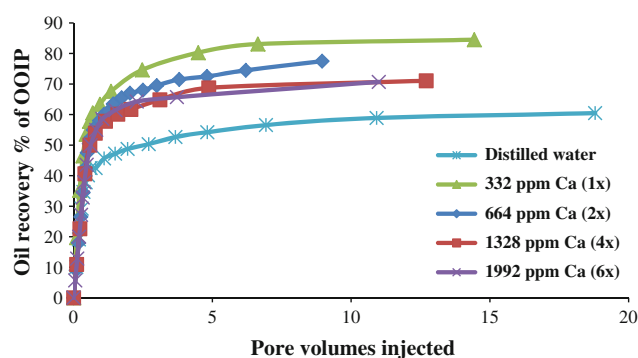
**Fig. 5** Oil recovery % of OOIP versus pore volumes injected of SW water with different salinity concentrations; *figure between brackets represent percent of dilution of original salinity concentration*



**Fig. 6** Oil recovery versus pore volumes injected brine at different  $SO_4^{2-}$  concentrations

the concentration of total dissolved solids of the synthetic brine in proportion to give sulfate content of 23.4, 46.8, and 70.2 ppm by adding  $Na_2SO_4$ . The ionic strength of these solutions was kept constant by adjusting the content of NaCl. The results of this set of experiments are shown in Fig. 6.

Figure 6 shows that with sulfate concentration of 46.8 ppm (four times the original sulfate concentration in the UER water) the highest oil recovery of 87.2 % of the OOIP was achieved. The sulfate concentration of 70.2 ppm (six times the original sulfate concentration) resulted in the lowest oil recovery of 61.5 % of the OOIP which is comparable to the distilled water of 60.5 % of the OOIP. Figure 6 also shows that increasing the sulfate concentration in the brine solution could increase the oil recovery until a critical value of sulfate concentration is reached above which oil recovery decreased. Similar trends were observed by Webb et al. (2005). In their study, they compared oil recovery from a North Sea carbonate core samples using sulfate-free formation simulated brine with seawater, which contains sulfate. The final results showed that the simulated seawater was able to increase the recovery by 20 percent. There is no clear evidence on the critical sulfate concentration in the literature.



**Fig. 7** Oil recovery versus pore volumes injected brine at different  $Ca^{2+}$  concentrations

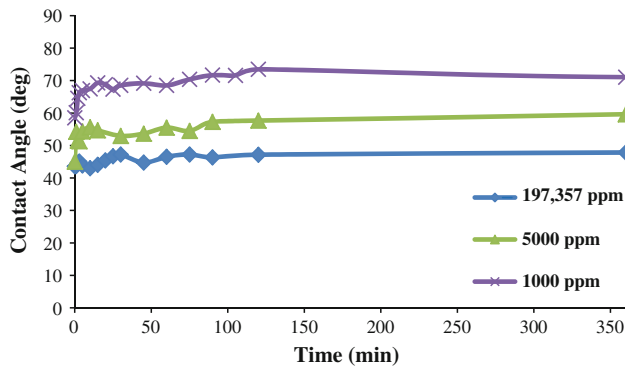
The second set of experiments in this section involved flooding core samples with UER water at 5,000 ppm containing calcium concentrations of 332, 664, 1,328, and 1,992 ppm, respectively. Brine concentration was varied by changing the concentration of total dissolved solids of the synthetic brine in proportion to give brine of 664, 1,328, and 1,992 ppm of calcium content by adding  $CaCl_2$ . The ionic strength of these solutions was kept constant by adjusting the content of NaCl. The results of this set of runs are shown in Fig. 7.

Figure 7 shows that calcium concentration has a negative effect on oil recovery. Flooding with the original calcium concentration of 332 ppm yielded the highest oil recovery and by increasing the calcium concentration the oil recovery decreased. The MIE (multicomponent ionic exchange) concept that was proposed by Lager et al. (2008) and the Double layer effect that was suggested by Ligthelm et al. (2009) indicates that calcium plays a key role in the oil recovery process in the presence of clay. In this work, however, it is shown that in clay-free core samples, flooding with calcium could have a negative effect on oil recovery.

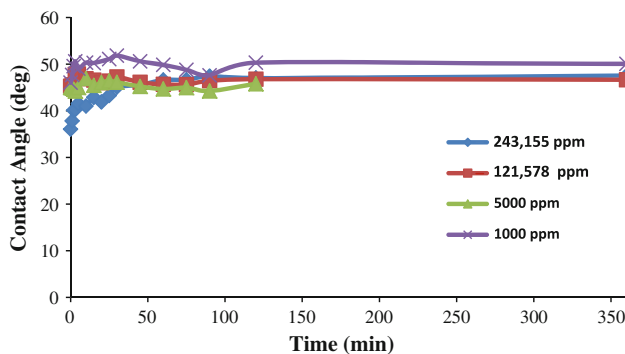
#### Contact angle measurements

The results of the sessile drop method were analyzed with Sigma Scan Pro image analysis software to determine the change of contact angle measurements with time. The results of these measurements for the oil-UER brine-rock, oil-SIM brine-rock, and oil-SW-rock systems considered in this work are illustrated in Figs. 8, 9, and 10, respectively.

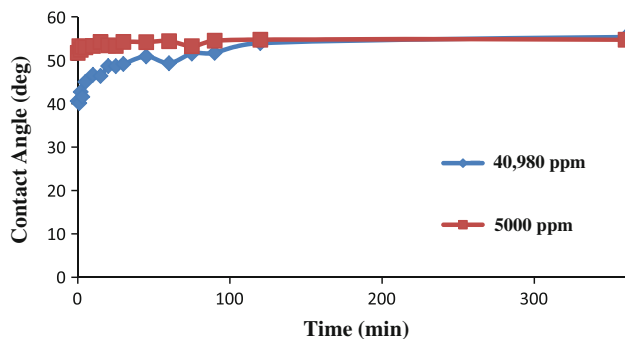
The repeatability of the contact angle measurements was evaluated by calculating the percent deviation of a certain reading from the preceding value. The maximum deviation observed was approximately 1.37 % which could be partially attributed to machine error. The early time fluctuations were observed in all the experiments of contact angle measurements. These fluctuations are believed to be attributed to the continuous change in the shape of the oil



**Fig. 8** Results of contact angle measurements for UER water and its corresponding diluted solutions

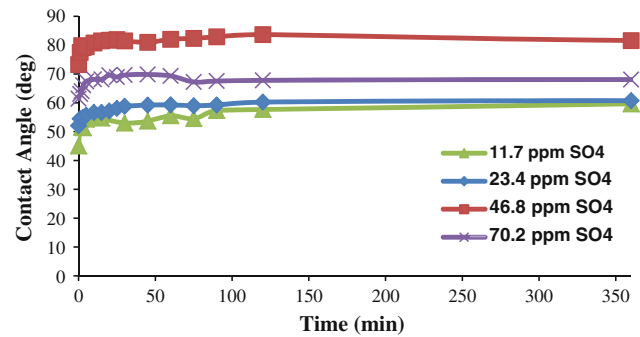


**Fig. 9** Results of contact angle measurements for SIM water and its corresponding diluted solutions

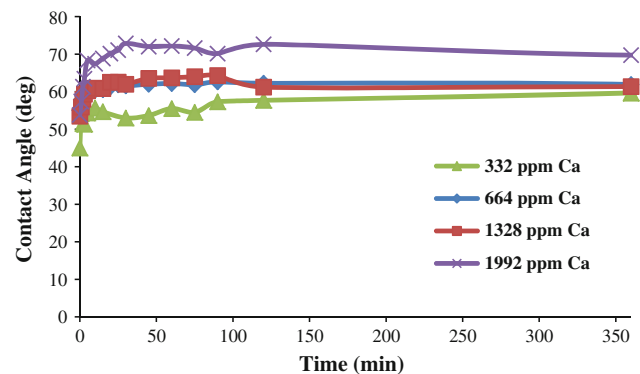


**Fig. 10** Results of contact angle measurements for SW water and its corresponding diluted solutions

drop observed during the early time of the experiments. Once the shape of the oil drop reached a stabilized state, the fluctuations disappeared and a stable value of contact angle was observed for the rest of the experiment. Although not shown in Figs. 8, 9, 10, 11, and 12, each contact angle measurement was allowed to continue for 650 min to make sure that stabilization has been reached. Thus, it can be deduced that the fluctuations did consume some 20 % of the testing time.



**Fig. 11** Contact angle measurements for different  $\text{SO}_4^{2-}$  concentrations



**Fig. 12** Contact angle measurements for different  $\text{Ca}^{2+}$  concentrations

The results of contact angle measurements presented in Figs. 9 and 10 and the results of core flooding tests presented in Figs. 4 and 5 indicate that oil recovery could increase if the contact angle is increased. In other words, the oil recovery could increase as the wettability is changed to more intermediate levels. This observation is in contradiction with Jadhunandan and Morrow (1995), Tang and Morrow (1999a, b), Zhang and Morrow (2006); they all concluded that water-wet wettability yields higher oil recovery. Agbalaka et al. (2008) conducted a review on the effect of reservoir rock wettability on oil recovery for secondary and tertiary oil recovery processes. Several field cases as well as laboratory studies were discussed. The fact that wettability affects oil recovery can affect oil recovery efficiency is widely acknowledged. However, the wetting phase that will result in optimal recovery of oil has been the subject of intense debate. Agbalaka et al. (2008) observed that the reason for this divergence in observed reports is attributable to a number of factors which includes (1) difficulty in wetting state reproducibility, (2) lack of unified standards and procedure for coring, core handling and core storage, and (3) the wetting state characterization method adopted. They concluded that strongly oil wet reservoirs give the least oil recovery and the best recovery



appears to be the intermediate wet reservoirs. These findings are consistent with the results of the present work. Sharma and Filoco (2005) also suggested that low-salinity brine changes the wetting properties of the rock surface from water-wet to mixed-wet and thereby increase the recovery.

Figure 10 shows that there is hardly any change in the contact angle between the original SW brine and the 5,000-ppm solution of the SW brine. This observation may explain the results presented earlier in Fig. 5 where

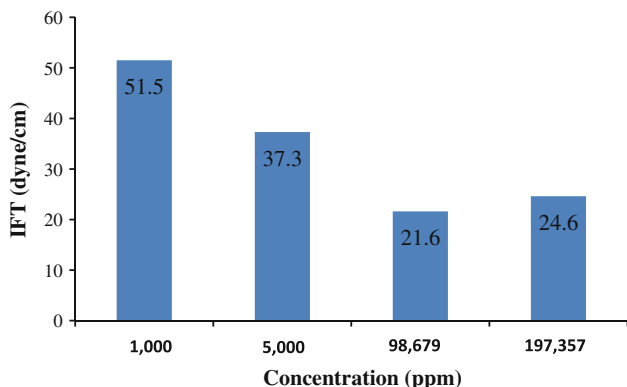


Fig. 13 Results of IFT measurements for UER brines and its diluted samples

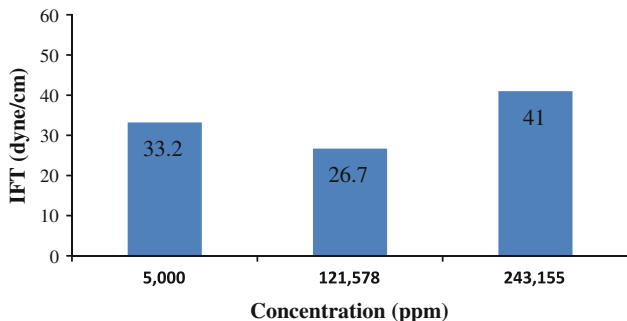


Fig. 14 Results of IFT measurements for SIM brines and its diluted samples

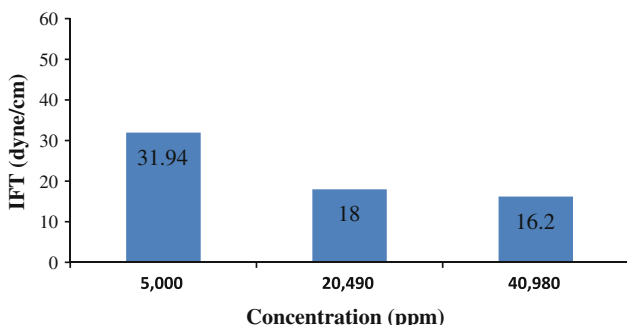


Fig. 15 Results of IFT measurements for SW brines and its diluted samples

flooding with low-salinity flooding SW has no effect on the oil recovery. Also shown in Fig. 5 that the oil recovery performances in the three runs including distilled water are comparable.

In order to investigate the effect of changing the ionic composition on wettability, eight brines with different concentration of  $Ca^{2+}$  and  $SO_4^{2-}$  were used. The  $Ca^{2+}$  concentration ranges from 332 to 1992 ppm. The  $SO_4^{2-}$  concentration ranges from 11.7 to 70.2 ppm. Figures 11 and 12 show the results of the contact angle measurements for different  $SO_4^{2-}$  and  $Ca^{2+}$  concentrations, respectively.

Figure 11 shows that the highest angle of contact was observed at 46.8 ppm concentration of  $SO_4^{2-}$ . This

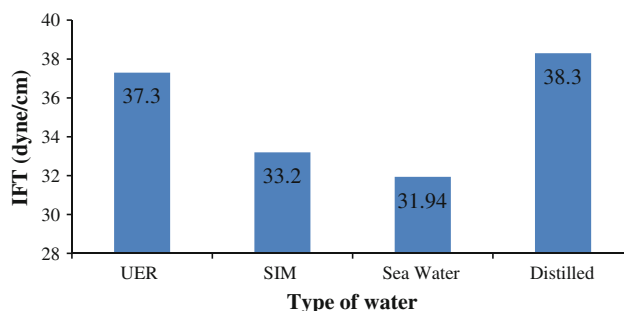


Fig. 16 Results of IFT measurements for UER, SIM and SW brines at 5,000 ppm dilution

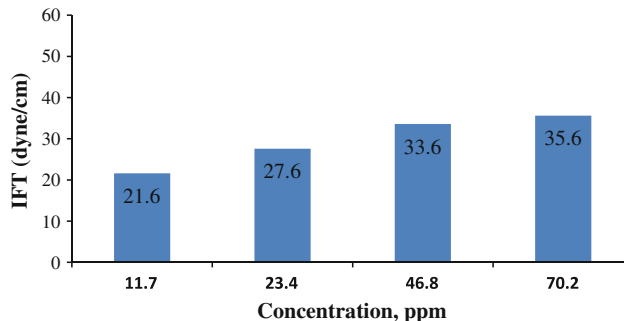


Fig. 17 Results of IFT measurements for different  $SO_4^{2-}$  concentrations

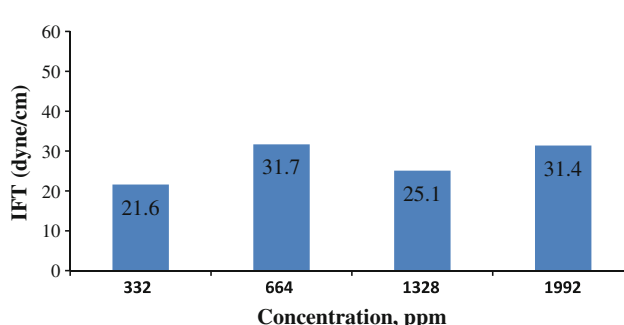
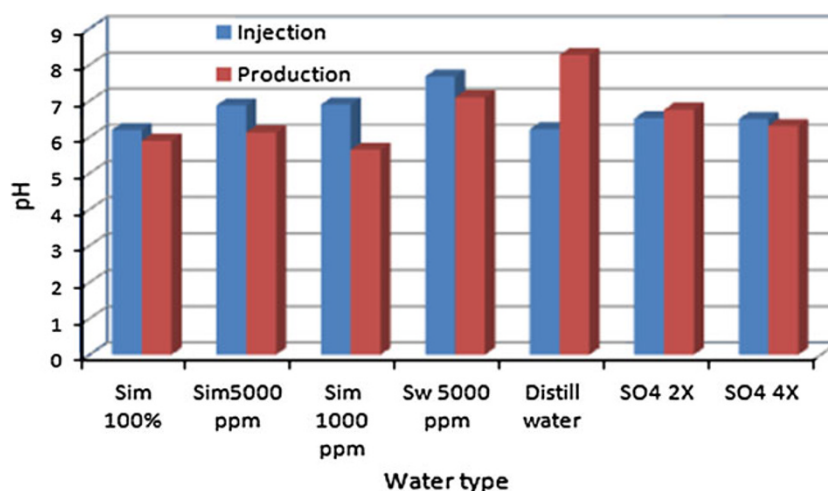


Fig. 18 Results of IFT measurements for different  $Ca^{2+}$  concentrations

**Fig. 19** Results of pH measurements for different brines



observation could explain the results of Fig. 6 as the 46.8-ppm concentration of  $\text{SO}_4^{2-}$  yields the highest recovery and confirms the results of Agbalaka et al. (2008). These authors concluded that the best recovery appears to be achieved in the intermediate wet reservoirs. Zekri et al. (2011) investigated the effect of EOR techniques on wettability and oil recovery of carbonate and sandstone formation. They concluded that increasing the sulfate concentration in the injection brine changed the wettability of the chalky and microcrystalline limestone used in their experiments into more water-wet.

#### IFT measurements

Interfacial tension measurements (IFT) were conducted with the interfacial tensiometer using Bu Hasa crude oil and different brines to assess the effect of IFT on the mechanism of low-salinity flooding. All measurements were carried out at room temperature of 25 °C and the results of these tests are illustrated in Figs. 13, 14, 15, 16, 17, and 18.

No systematic trend on the effect of  $\text{Ca}^{2+}$  on IFT measurements was observed in this work and this may explain the high oil recovery with the lowest concentration of  $\text{Ca}^{2+}$  that exhibited lowest value of IFT. The results also indicate that there is an optimum salinity for different tested brines but the observed optimum salinity does not correlate with the optimum oil recovery by low-salinity flooding. Therefore, interfacial tension may not be responsible for the increase in oil recovery due to the injection of low-salinity water. This observation contradicts the results of Okasha and Al-Shiwaish (2008) who investigated the effect of brine salinity on interfacial tension in Arab-D carbonate reservoir in Saudi Arabia. He concluded that the reduction of IFT with brine dilution reflects the potential implication of low-salinity flooding in improving oil recovery.

No fluctuations were observed in the IFT measurements and excellent repeatability of selected measurements was noted.

#### pH measurements

Some studies have shown a rise in pH during low-salinity flooding experiments. This rise in pH is due to two reactions: carbonate dissolution and cation exchange. The dissolution of carbonate (i.e., calcite and/or dolomite) results in an excess of  $\text{OH}^-$  and cation exchange occurs between clay minerals and the invading water. The dissolution reactions are relatively slow and dependent on the amount of carbonate material present in the rock (Lager et al. 2006). Conflicting evidence throws doubt on this mechanism being the cause of the low-salinity flooding effect. The results obtained from the core flooding experiments and pH measurements of this study indicate no correlation between the pH variation and improved oil through low-salinity flooding as shown in Fig. 19. Therefore, high pH may not be responsible for the increase in oil recovery with low-salinity waterflooding.

#### Conclusions

Based on the results of the experimental work conducted in this study the following conclusions may be drawn:

1. Low-salinity flooding seems to have good potentials in Bu Hasa field.
2. Contact angle measurements indicate that lowering the solution salinity could shift the wettability of the system towards intermediate levels and this effect appears to be responsible for the improved oil recovery.
3. Increasing the  $\text{Ca}^{2+}$  concentration in the injected brine resulted in decreased ultimate oil recoveries.

4. Increasing the  $\text{SO}_4^{2-}$  concentration in the injected brine tends to change the wettability to more intermediate levels and resulted in improved ultimate oil recoveries. However, there is an optimum  $\text{SO}_4^{2-}$  concentration of 46.8 ppm in the 5,000 ppm UER which resulted in highest oil recovery. It is believed that this optimum concentration of  $\text{SO}_4^{2-}$  in the flooding tests is responsible for shifting the system's wettability to intermediate water-wet.
5. The IFT of the oil-brine system may not have a direct effect on low-salinity flooding overall performance.

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