



Eliminate the role of clay in sandstone: EOR low salinity water flooding

Hasan N. Al-Saedi^{1,2} · Ralph E. Flori¹ · Soura K. Al-Jaberi²

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Abstract

Low-salinity (LS) water flooding mechanism enhanced oil recovery (EOR) method in sandstone has been extensively debated in the literature. Many mechanisms have been proposed, but these proposed mechanisms remain a topic of debate. In this study, we propose to quantify control of mineral composition and water chemistry on water/rock interactions and wettability change during low-salinity waterflooding of spatially heterogeneous sandstone porous media. We intended to identify the dominant process of wettability alteration through considering water–rock interaction mechanisms containing/non-containing clays. Water chemistry partially determines the dominant wettability alteration. This includes salinity, type of ions, and possibly pH. Sandstone core and free clay sand core were prepared in chromatography columns and were water flooded with high/low/high-salinity water at different temperatures. Brine with high salinity 100,000 ppm was injected to simulate formation water, then, inflow low-salinity water 1100 ppm at different temperatures. Concentrations of Ca^{2+} and CH_3COO^- and pH were recorded. The core contains quartz only, to investigate the role of clay in the mechanism of smart water EOR. The results proved that during flooding the free clay core by low-salinity water the carboxylic acid detached from the sand, albeit not as great as that of the clay-containing cores. On the other hand, ICP-OES showed a noteworthy desorption of Ca^{2+} from the free clay core surface. That indicates further RCOO^- recovery in the absence of clay. It has been observed that during flooding by LS water, the pH increased significantly. Also, as the temperature increased the pH of the LS water decreased and amount of Ca^{2+} decreased in the effluent. This work presents the results of forced imbibition experiments to examine the effect of clay in sandstone during LS flooding EOR.

Keywords LSWF · Cation desorption · Geochemistry · EOR

Introduction

Field pilots and laboratory tests conducted on sandstone have shown that incremental oil recovery can be attained by injecting low-salinity water. The mechanisms behind incremental oil recovery by low-salinity water are controversial. The suggested mechanisms of enhancing oil recovery/wettability alteration in sandstones include: mineral dissolution (Aksulu et al. 2012), multi-component ion exchange (Lager et al. 2008a, b), double-layer expansion (Ligthelm et al. 2009), desorption of organic material from clay surfaces (Austad et al. 2010), reduction in interfacial tension

(McGuire et al. 2005), and fines migration (Tang and Morrow 1999). Production apparently depends on the presence of clays in the reservoir (Lager et al. 2008a, b; Ligthelm et al. 2009; Austad et al. 2010; McGuire et al. 2005; Tang and Morrow 1999). The chemical composition of the injected water is another controlling parameter (Austad et al. 2010; Rezaeidoust et al. 2009; RezaeiDoust et al. 2011). However, there is no consensus on the dominant recovery mechanism (Austad et al. 2010; RezaeiDoust et al. 2011; Nasralla et al. 2013). This may be because several simultaneous processes contribute to the overall process. To our knowledge, no systematic experimental and numerical studies have been carried out that consider the most important water–rock interactions in sandstones simultaneously.

Reservoir chemical heterogeneity may also play a role. Experimental and field scale projects indicate that incremental oil recovery by low-salinity (LS) water flooding vary significantly case-by-case in both carbonates (Zhang et al. 2007; Yousef et al. 2012) and sandstones (McGuire et al.

✉ Hasan N. Al-Saedi
hnav36@mst.edu

¹ Department of Geosciences and Geological and Petroleum Engineering, Missouri University of Science and Technology, Rolla, MO 65401, USA

² Missan Oil Company, Missan, Amara 62001, Iraq

2005; Lager et al. 2008b). Minerals in natural porous media are typically distributed unevenly with random spatial patterns, ranging from uniform distribution to clustered minerals (Barber et al. 1992; Zinn and Harvey 2003). On one hand, physical heterogeneity changes flow fields and, therefore, spatial distribution of ions (Heidari and Li 2014). On the other hand, chemical heterogeneity significantly changes mineral dissolution rate (Salehikhoo et al. 2013; Li et al. 2014) and adsorption/desorption (Wang and Li 2015). Combination of physical and chemical heterogeneity can significantly impact water–rock interaction and wettability alteration. However, the effect of spatial distribution of reservoir physical and chemical properties on water–rock interaction and wettability alteration during LS water flooding has not been fully considered.

It was believed that the adsorption/desorption of organic materials occurred only on the negative sites of the clays in sandstone (Austad et al. 2010; RezaeiDoust et al. 2011; Fogden 2012). The experimental observations of Tang and Morrow (Austad et al. 2010) suggested conditions for chemical mechanisms for enhanced oil recovery by LS water flooding, those conditions are: (1) clay must exist in the sandstone core and (2) crude oil must contain organic materials. Lager et al. (2006) add another condition which was (3) active ions such as Ca and Mg must present in the formation water. In this study, we investigate the role of the clay in the sandstone and its effect on LS water enhanced oil recovery (EOR).

We examine the mechanism(s) of LS waterflooding in sandstone with and without clays as a function of temperature using three chromatographic columns containing different percentages of quartz and clays. The columns were flooded with high-salinity (HS) brine (~100,000 ppm) until a constant pH was noted. The injecting water was then exchanged to LS water (~1000 ppm). The effluent was collected for Ca^{2+} and CH_3COO^- chemical analyses.

Methodology

Materials

Column packing

Chromatography columns were packed with quartz for the sand column and with quartz and clays for sandstone column. To avoid air bubbles in the column, which can change the hydraulic conductivity, wet packing was done (Minyard and Burgos 2007). The connections to the column ports were configured with a fine filter to prohibit mineral grains moving out of the column (Fig. 1).

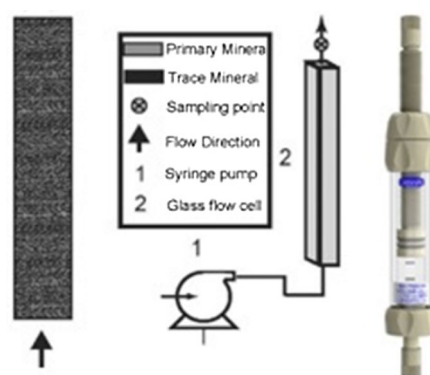


Fig. 1 Flow cell schematic

Table 1 Brine composition (PPM)

Element	HS	LS
Na^+	35,000	350
Cl^-	60,000	600
Ca^{2+}	4500	0
Acetate	820	0
TDS	98.32	1.182
Salinity	~100,000	~1000

Brines

Two kinds of brine were used in this study, HS and LS water. HS brine was prepared by liquefying reagent CaCl_2 and NaCl in deionized water, and LS water was prepared by dissolving reagent NaCl in deionized water. Brine compositions are listed in Table 1.

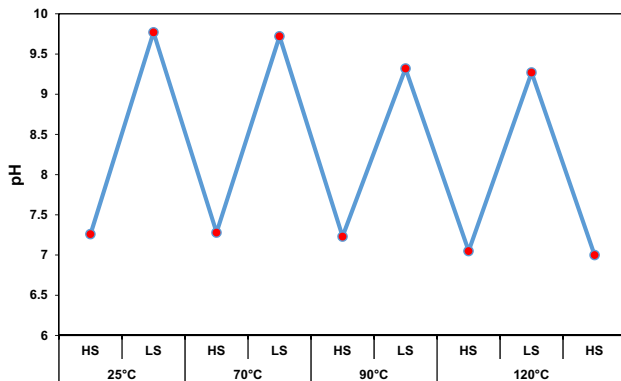
Experimental procedure

Column water flooding in the presence of acetate

The column was flushed by HS water and then aged for a week at 70 °C with the same HS water containing 10 mmole sodium acetate. This was done to maximize sorption of carboxylic material to the surface of the rock so as to simulate bonding of oil-bound carboxylic material to a reservoir. The system was then flooded with HS water until the pH stabilized. Brines were pumped upward from the bottom of the columns using a syringe pump. Aqueous samples were collected at the column outlet for later analysis of ionic concentrations. After each experiment, the column was aged at the same condition for a week to restore the sample to the initial conditions. The whole system was operated inside an oven set to the temperature of interest (Table 2).

Table 2 Description of the columns

Quartz (%)	Illite (%)	Kaolinite (%)	<i>D</i> (cm)	<i>L</i> (cm)	<i>K</i> (md)	Φ (%)
100	0	0	1.5	6.3	600	33.6
80	20	0	1.5	6.3	301	33.24
80	0	20	1.5	6.3	65	33.02

**Fig. 2** Effluent pH from sand column, at 25, 70, 90, and 120 °C

Chemical analysis

Ca²⁺ concentrations were measured using (2000D ICP-OES). Effluent acetate concentrations were measured using a Dionex DX-120 ion chromatography setup.

Oil recovery test

The same columns were flushed and saturated with HS water and then flooded with crude oil and aged for a week at 70 °C. HS water then injected into the column followed by LS water and oil recovery was observed from the effluent.

Results and discussion

Sand column

This column was 100% quartz. At 25 °C (Fig. 2), the pH was 7.26 when flooded with high-salinity water. Upon switching to LS water the pH rose to pH 9.77. When the injected water was transferred to the original HS water, the pH fell back to 7.29. There was about a 2.5 pH difference between HS water effluent pH and LS water effluent pH. The upward shift in effluent pH difference between HS and LS water is traditionally ascribed to the exchange of H⁺ for Ca²⁺ on clay surfaces (Lager et al. 2006). We observe the same trend in the absence of clay and ascribe it to H⁺ exchange for Ca²⁺ and Na⁺ sorbed to negatively charged quartz surface sites.

At 70 °C, the pH for the HS water effluent was 7.28. The water then switched to the LS water and pH for the LS

water effluent was 9.72. After that, switching the flooding to the original HS water stabilized the pH back to its original value. An important variance ~2.44 in pH between HS water and LS water effluents was observed. The pH trend is about the same at 90 °C. The pH stabilized at 7.23 while flooding the column by HS water, after switching to LS water the pH increased directly and stabilized at 9.32. The injected fluid switched again to the original HS water and pH return to its original value. At 120 °C, the pH initially was 7.15 when flooded Column 1 by HS water. The pH suddenly rose and stabilized at 9.20 pH unit when switching the flooding to LS water. The injected fluid then switched again to the same HS water, and the pH fluctuated until fell again to its original value.

At all temperatures, evidence for Ca²⁺ desorption is seen in Fig. 3. It does not appear to be a clear trend after 90 °C. As can be seen from (Table 1) that LS water has no Ca²⁺.

The desorbed Ca²⁺ in the exchanger attributed to the ion exchange of Ca²⁺ with H⁺ and Na⁺ on the negative surface site of quartz. Figure 4 shows effluent acetate profiles from cores that were aged in HS water containing 10 mmole sodium acetate for a week at 70 °C (Fig. 5).

Again, core aging in acetate was done to maximize sorption of carboxylic material to the surface of the rock to simulate the bonding of oil-attached carboxylic groups to reservoir surfaces. It should be noted that Fig. 4 is plotted for the whole pore volumes that were injected to clarify the total volume that injected into the Sand Column. Figure 4 shows a lack of correlation between increasing temperature and detachments of carboxylic materials when flooding the column by HS and LS water. As can be noticed, the detachment of RCOO⁻ was higher at 25 °C than at 70 °C which was less than what was observed at 90 °C and the least detachment was at 120 °C. However, a significant carboxylic material was produced when switched the fluid to LS water especially at 25 °C and 90 °C.

In conclusion, it is obvious that quartz surface and carboxylic materials are both negatively charged, so carboxylic materials repelled from the quartz surface. Indeed, the carboxylic material bonded with multivalent cation Ca²⁺ [–COOCa⁺] [> SiO₂–] in form of electrostatic bridging with quartz surface. When LS water invaded the porous media, an ion exchange takes place then organic complexes removed and replaced with uncomplexed cations providing a more water wet environment and in turn enhancing recovery. In another word, when LS water invaded sand

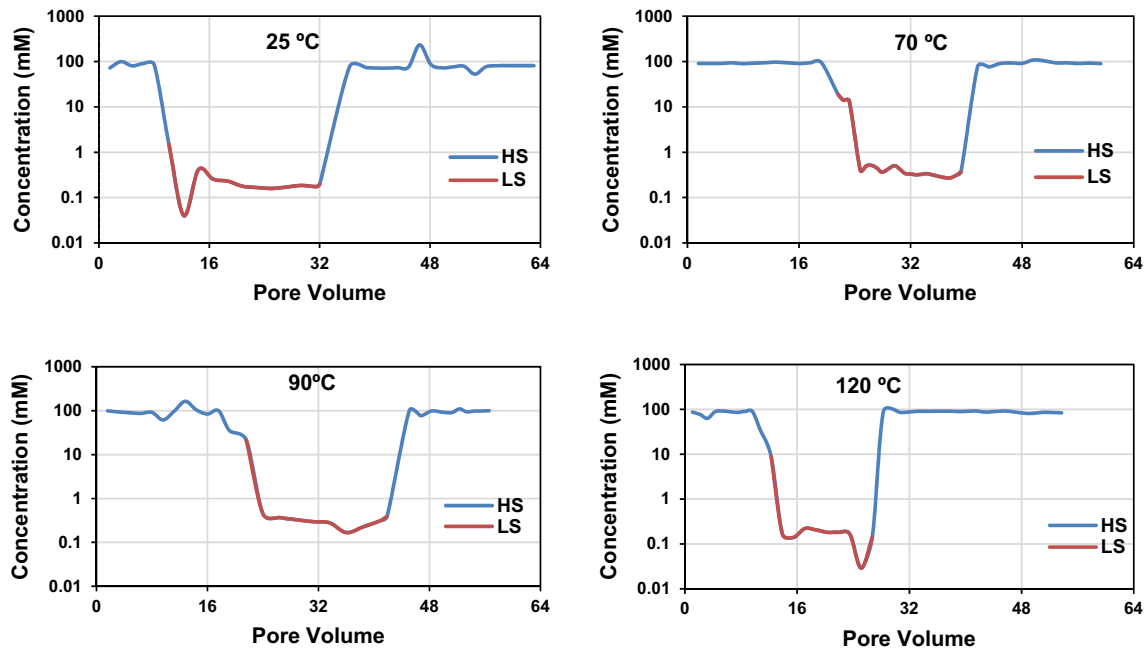


Fig. 3 Effluent concentrations of Ca^{2+} from sand column at 25, 70, 90, and 120 °C

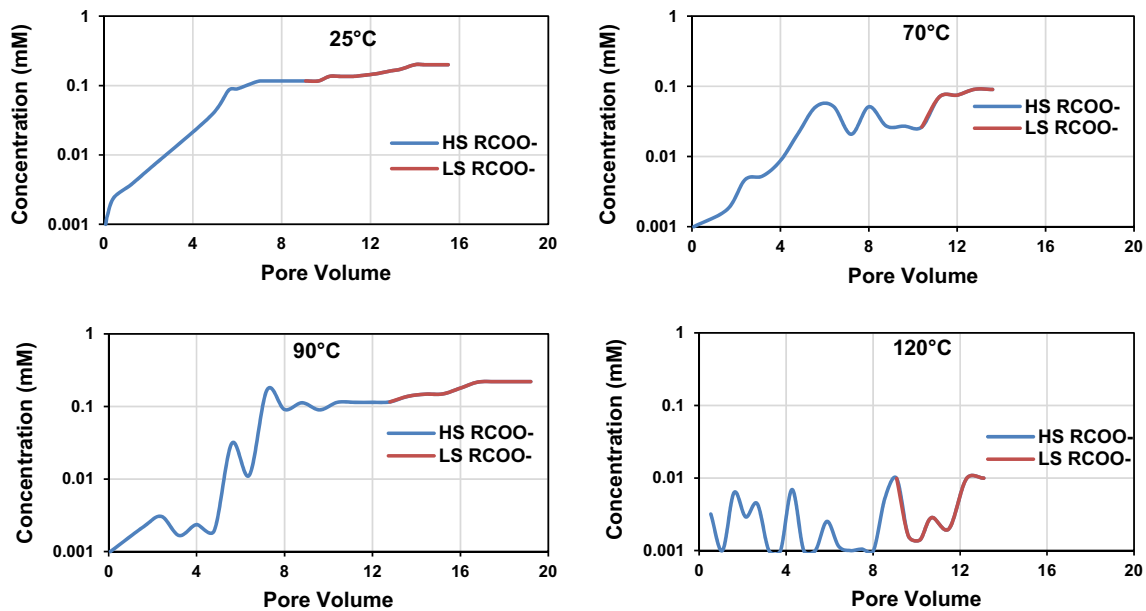


Fig. 4 Concentrations of RCOO^- in first HS and LS water effluent at 25, 70, 90, and 120 °C

column, the electrostatic attraction between the linked carboxylic on Ca^{2+} [$-\text{COOCa}^{2+}$] and [$>\text{Si-O}_2^-$] became very weak and the recovery increased. A quite clear correlation observed for the pH gradient, as the temperature

increased the pH gradients decreased. The gradients of pH were 2.51, 2.44, 2.09, and 2.04 at 25, 70, 90, and 120 °C, respectively. ICP-OES shows that about 0.32, 0.37, 0.32, and 0.16 $\mu\text{mole Ca}^{2+}$ desorbed from silicate surface at 25,

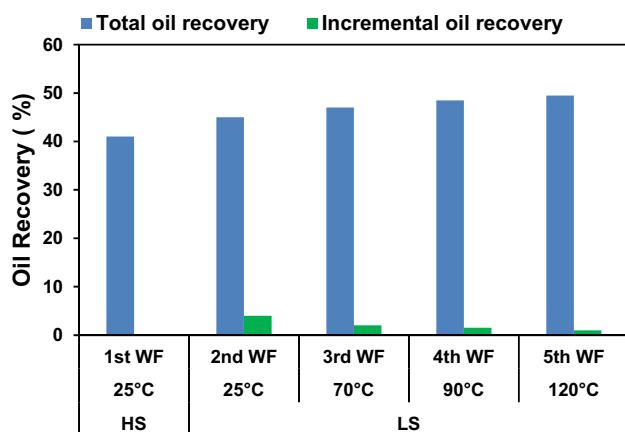
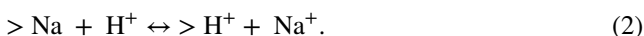
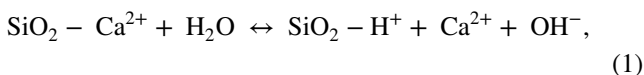


Fig. 5 Oil recovery test for sand column

70, 90, and 120 °C, respectively, when the flooding fluid switched to LSW effluent (Fig. 3). A significant amount of RCOO^- was produced when the water switched from HS to LS water. The acetate release was 10.60%, 8.35%, 3.80% at 25, 70, 90 °C, respectively, while the recovery curve was not stable at 120 °C (Fig. 4). This is a good evidence of how LS water improved the carboxylic acid detachment in sandstone without clay. The obtained results for Ca^{2+} desorption and RCOO^- detachment were in line with our expectations. The following reactions explain the ion exchange on the sand surface:



Oil recovery test (sand column)

The column was initially flooded by HS water at 25 °C until no oil recovery in the effluent; the oil recovery factor was 41% OOIP. The injected fluid then switched to LS water and the incremental oil recovery was 4% OOIP at 25 °C. The incremental oil recovery was 2, 1.5, and 1% OOIP at 70, 90, and 120 °C, respectively.

Sandstone column#1 (sand + illite)

The pH trend during flooding this column was approximately the same as quartz column (Fig. 6). The pH of HS water was around 7, and as the temperature increases, the pH

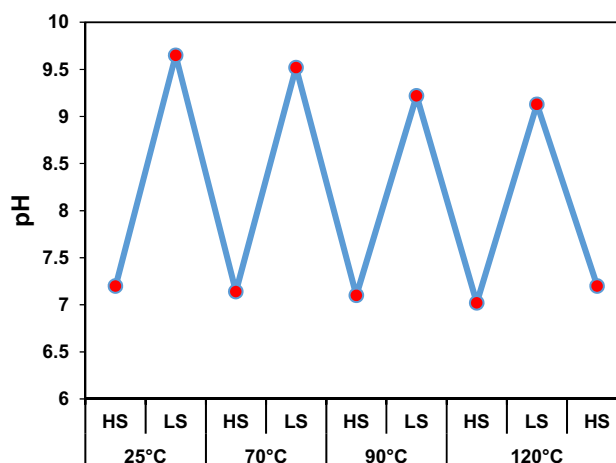


Fig. 6 Effluent pH from sand column#1 (sand + illite), at 25, 70, 90, and 120 °C

decreases. Upon switching to LS water, the pH jumped to 9.65, 9.52, 9.22, and 9.13 at 25, 70, 90, and 120 °C, respectively. The Ca^{2+} measurements from the effluent were performed the same way as in sand column, and the results were in line with the sand column. Ca^{2+} desorption occurred at all temperatures (Fig. 7). Acetate detachments were also approximately the same as in sand column (a little higher than the sand column) (Fig. 8), supported our theory about eliminating the clay role.

Oil recovery test (sandstone column#1)

The same procedure was conducted as in oil recovery test for sand column. The ultimate oil recovery during HS flooding was 42.23% OOIP at ambient temperature. Upon switching to LS water, the incremental oil recovery was 3.2, 2.3, 2, and 0.5% OOIP at 25, 70, 90, and 120 °C, respectively (Fig. 9).

Sandstone column#2 (sand + kaolinite)

The measurements Ca^{2+} desorption and acetate detachments from quartz and clay surfaces were in line with the two previous columns. Normally, pH decreased with the temperature increase except for this column. An increase in pH of the LS water effluent took place after switching to LS water due to the buffering effect of the high concentration

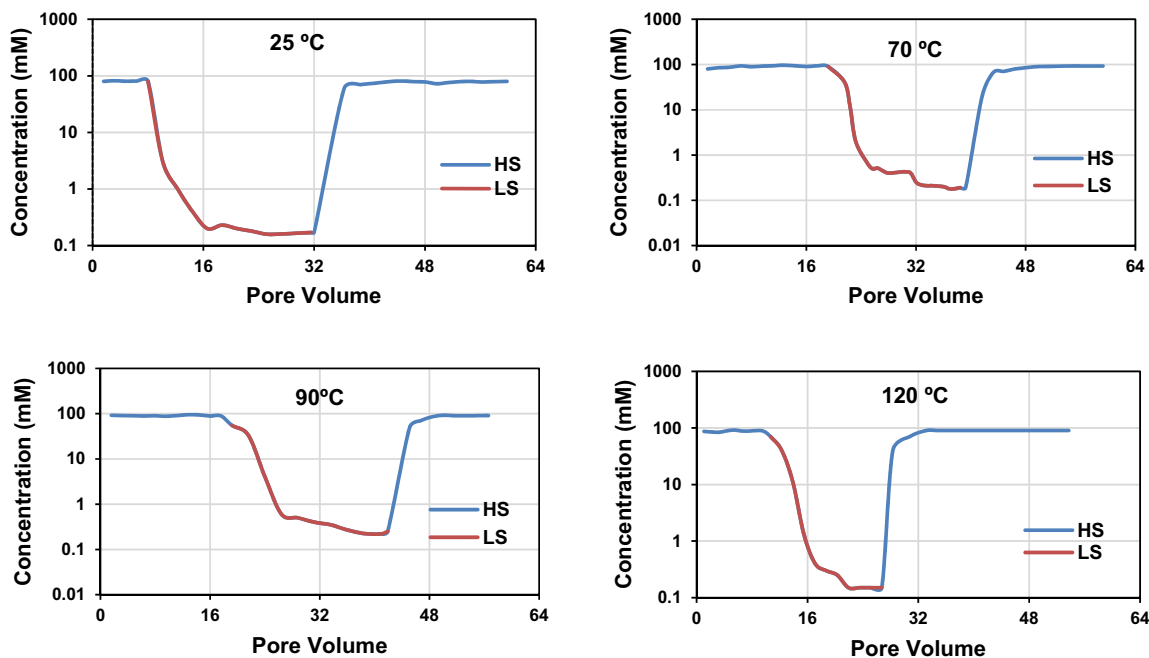


Fig. 7 Effluent concentrations of Ca²⁺ from sandstone column#1 (sand + illite), at 25, 70, 90, and 120 °C

of desorbed Ca²⁺ in sandstone column#2, which causes a local increase in pH $Ca^{2+} + OH^{-} \leftrightarrow (Ca-OH)^{+}$ (Rezaei-Doust et al. 2011). Figures 10, 11 and 12 show the results of pH measurements, Ca²⁺ desorption, and detachment of the acetate.

Oil recovery test (sandstone column#2)

The ultimate oil recovery was 40.35% OOIP after the column flooded with HS water. The recovery improved to 4.1, 1.9, 1.55, and 1% OOIP after flooding the column with LS water at 25, 70, 90, and 120 °C, respectively.

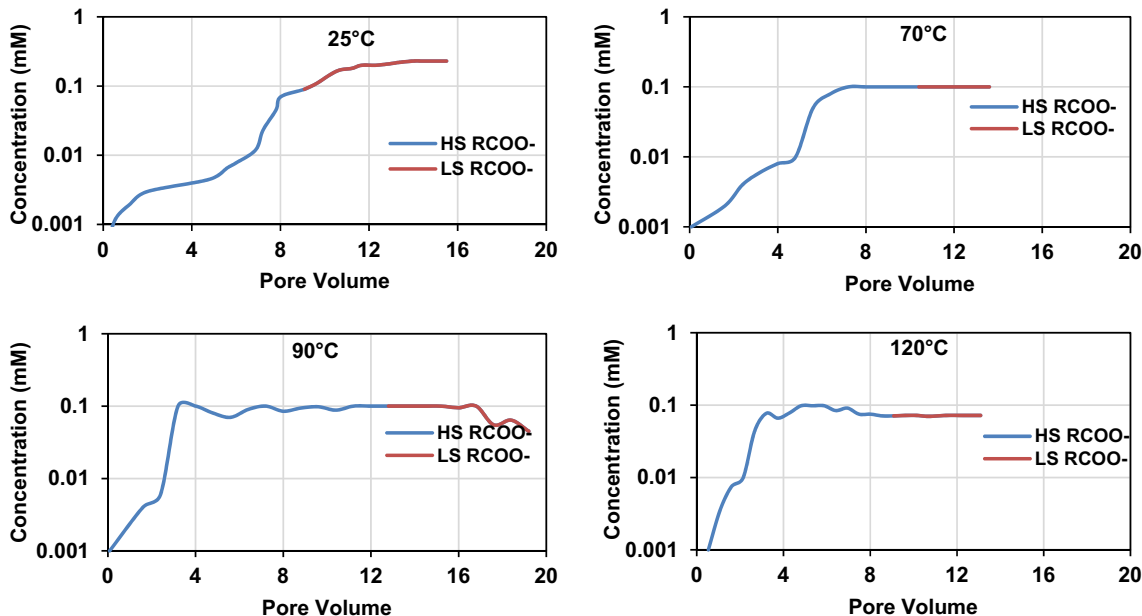


Fig. 8 Concentrations of RCOO⁻ in first HS and LS water effluent for sandstone column#1 (sand + illite), at 25, 70, 90, and 120 °C

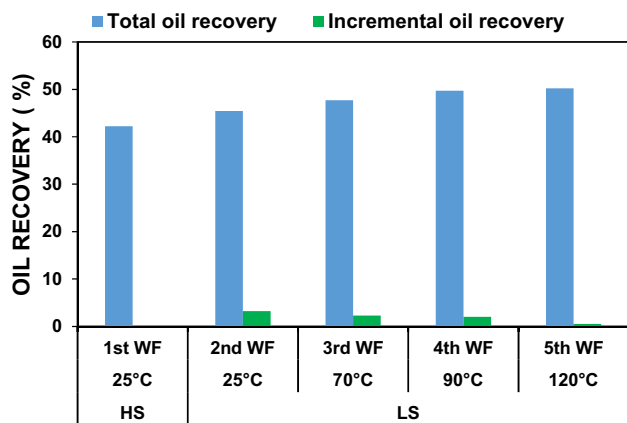


Fig. 9 Oil recovery test results for sandstone column#1 (sand + illite)

Figure 13 shows the oil recovery test results for sandstone column#2.

General comment

As can be seen from the results of the three columns, the desorption of Ca^{2+} , pH upward shift, acetate detachments (which represent carboxylic acid in crude oil), and oil recovery tests were all approximately the same, which were in line with our theory of eliminating the role of clay from the effective factors that affect LS water flooding EOR. Sohrabi et al. (2015) conducted a systematic study to exclude the clay role as we did in this study. The incremental oil recovery that they had in the absence of clay was attributed to the formation of the micelles stemming from oil/brine interaction. In our previous work (Al-Saedi, Hasan et al. 2018), we measured the wettability alteration after flooding quartz column and quartz + clay column, and the results were the wettability altered towards more water wet in both columns. LS water was able to trigger the wettability of sand the same way that occurred in the

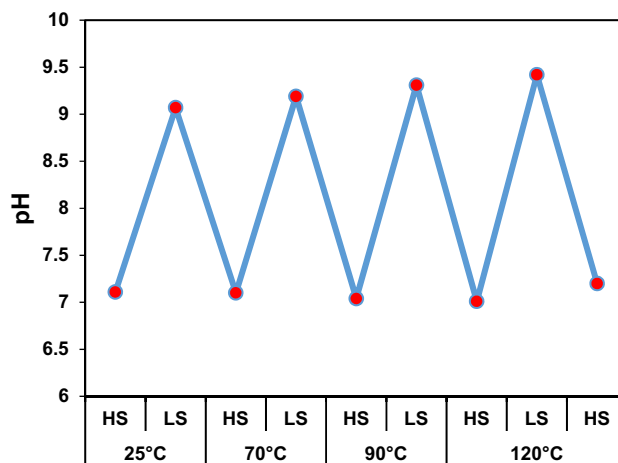


Fig. 10 Effluent pH from sand column#2 (sand + kaolinite), at 25, 70, 90, and 120 °C

presence of clays as shown in this reaction $[-COOCa^+][>SiO_2^-]$.

Conclusion

The approach of this work is investigating the mechanism of incremental oil recovery using LS water using three different porous media were packed in chromatographic columns. Our study results reveal the important role that clay play in LS water–sandstone/LS water–crude oil. This study can provide insights to researchers when designing the LS water flooding and help researchers to decode the chemical mechanisms that control LS water flooding in sandstone. Clays participate in some of the oil recoveries, but quartz behaved the same way as clay. The results show that acetate detachments/oil recovery increased during LS water flooding albeit in the absence of clay. In addition, pH and Ca^{2+} desorption from quartz surface was as high as in the presence of clays, indicating that an ion exchange occurred on the quartz surface.

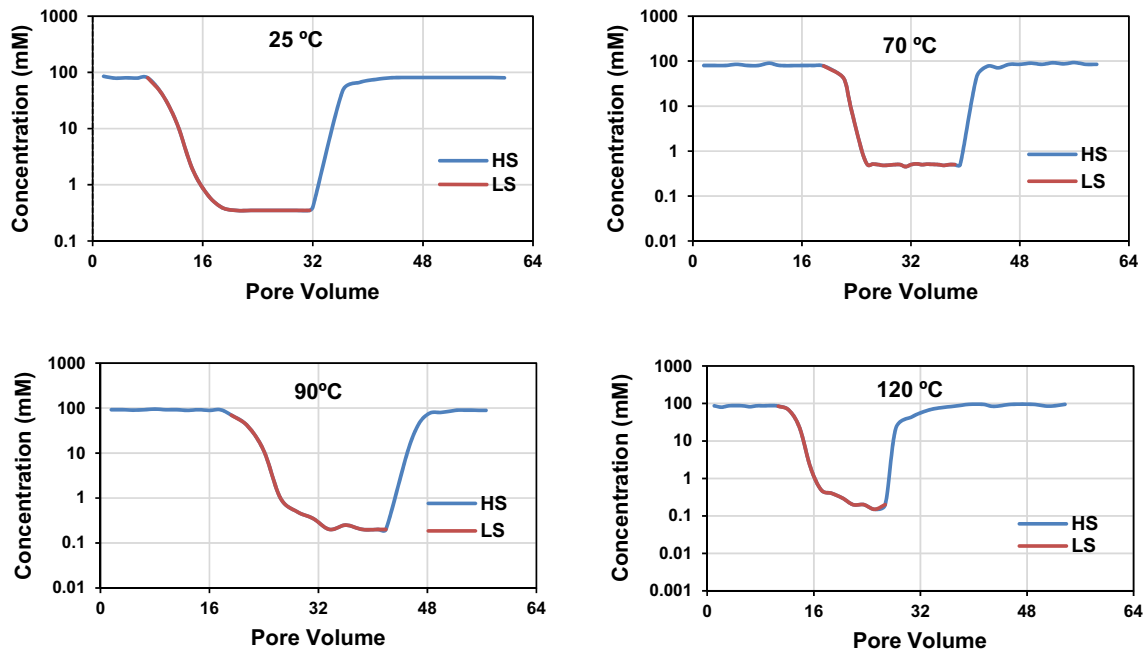


Fig. 11 Effluent concentrations of Ca^{2+} from sandstone column#2 (sand + kaolinite), at 25, 70, 90, and 120 °C

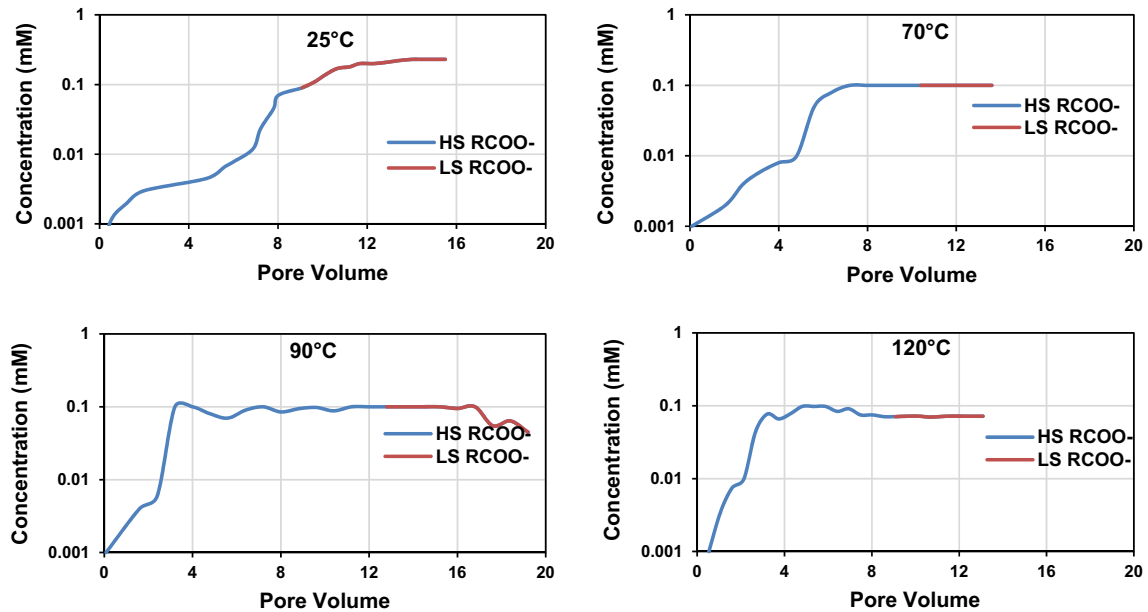


Fig. 12 Concentrations of RCOO^- in first HS and LS water effluent for sandstone column#2 (sand + kaolinite), at 25, 70, 90, and 120 °C

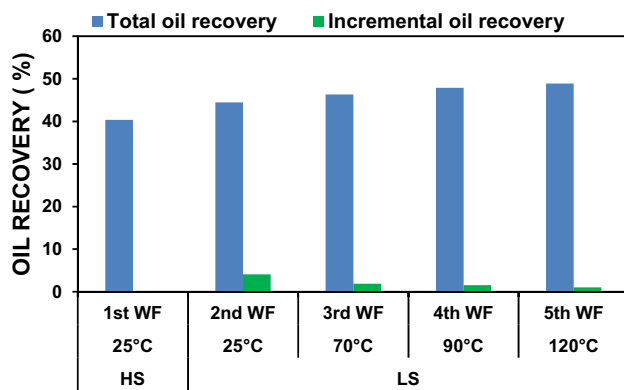


Fig. 13 Oil recovery test results for sandstone column#2 (sand + kaolinite)

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