Effect of temperature on the pH of water flood effluents and irreducible water saturation: A study with reference to the Barail sandstone outcrop of the upper Assam Basin

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Abstract

Low salinity water flooding (LSWF) is a promising strategy for improving oil recovery in sandstone reservoirs, and recent studies have shown that the recovery with low salinity water injection is a function of not only the salinity and ionic composition but also of the pH of injected brine, temperature, and the combined effect of both on the wetting properties of the clay mineral surfaces. Following brine flooding, the initial wettability of sandstone rock surfaces existed when crude oil, formation water (FW), and rock surface interaction were in chemical equilibrium at reservoir condition changes based on brine pH, salinity, temperature, and clay mineralogy. This study proposes pH, core flood temperature, and irreducible water saturation as key parameters in inducing wettability changes in the sandstone porous media. In the present work, the sandstone cores were subjected to flooding at temperatures of 70 °C, 85 °C, and 105 °C and measured the pH of the discharge effluents and initial or irreducible water saturation with respect to varying temperatures. This paper investigates the rise of the pH gradient and irreducible water saturation, S_{wir} with respect to LS flooding, at increasing temperatures using a Barail sandstone core. The key results include the following:

- The pH of the flood effluents increases with increasing core flood temperature, which indicates a shifting of the existing wetting state of the rock.
- The combined effects of increasing pH and initial or irreducible water saturation pertaining to low salinity flooding at progressively increasing temperatures result in increasing water wettability of the sandstone rock. Increasing flooding temperatures cause an increase in S_{wir} , which follows a linear relationship.

The findings of the paper highlight the link of increasing pH and irreducible water saturation with the water wetting properties of the sandstone reservoir rock and hence the fluid flow or the oil–water relative permeability behaviour. This paper proposes that increased irreducible water saturation and pH of water flood effluents are connected to increasing water wetness in a sandstone rock as a function of elevated temperatures. As adequate work and consensus on the potential effects of temperature on wettability alteration under low salinity water flooding is still lacking, the current work in relation to the Barail sandstone of the upper Assam basin could be a novel reference for understanding of the importance of temperature dependent wettability alteration behaviour in sandstone cores. The findings of this study can assist in the formation of a novel approach towards considering the increasing irreducible water saturation and pH of the brine effluent as an effect of alternatively injection of low salinity water at elevated temperatures on sandstone porous rock.

Keywords Water flooding · pH · Reservoir temperature · Initial water saturation · Sandstone rock

List of symbols

S_{wir}	Irreducible water saturation
k_{ro}	Relative permeability to oil
LSWF	Low salinity water flooding
T	Temperature
k_{ro}, k_{rw}	Oil and water relative permeability
S_{wi}	Initial water saturation

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S_{wir}	Irreducible water saturation
T_A	Aging temperature
S_{or}	Residual oil saturation
S_{rw}	Residual water saturation
S_{wc}	Connate water saturation
k_w	Effective permeability to water
FW	Formation water
Wt. %	Weight percentage
μ	Viscosity
AN	Acid number
BN	Base number
PV	Pore Volume
pH	Potential of Hydrogen
°C	Degree Celsius

Introduction

The changes in reservoir wettability are caused by the crude oil-rock-brine interaction that occurs during all water flooding operations. The brine composition, initial water saturation (S_{wi}), and ageing temperature, T_A (°C), all have an impact on this interaction. The interaction induced by the surface-active elements of crude oil is principally responsible for any changes in the reservoir rock's wetting condition. The higher the ageing temperature, the greater the effect on the wettability of sandstone rock reservoirs (Jadhunandan & Morrow, 1995). Furthermore, the salinity, pH, and ionic concentration of the brine water to be flooded are critical parameters for any wettability changing behaviour of the sandstone rock. The more spatial heterogeneity there is, the less change there is in the wettability of sandstone rock surfaces. The interaction of minerals (quartz, illite, and kaolinite) causes the pH of flood water to rise at increasing reservoir temperature (Al-Saedi et al., 2019). In the case of low salinity water flooding, the pH of the flood effluent decreases significantly as reservoir temperature exceeds, particularly > 100 °C, rendering the water flood process incapable of increasing oil recovery. Water flooding in reservoirs with temperatures less than 100 °C, on the other hand, results in significant desorption of polar components from the clay surfaces. The sandstone rock becomes extremely water-wet as a result of this desorption (Piñerez et al. 2016). As the temperature increases, so does the flow capability and relative permeability of oil and water. Furthermore, the irreducible water saturation increases linearly, whereas the remaining oil saturation decreases nonlinearly. The relative permeability curve of the two-phase flow area, on the other hand, increases dramatically as temperature increases (Qin et al., 2018). Furthermore, the temperature dependency of oil–water relative permeability is a function of its water saturation; if the minimum water saturation surpasses 55%, the water–oil relative permeability ratio is temperature

insensitive (Davidson, 1969). The water–oil relative permeability ratio increases with increasing temperature in unconsolidated sand with low residual oil saturation, but decreases in consolidated rock with increased residual oil saturation. Beyond a critical temperature, however, an increase in temperature has little effect on displacement (Ehrlich, 1970). For sandstone rock, increased flood temperature causes a rise in irreducible water saturation, an increase in relative permeability to oil and water at flood-out, and a decrease in the water–oil relative permeability ratio. Furthermore, when temperature increases, the absolute permeability of the sandstone core diminishes (Weinbrandt et al., 1975). However, a contradictory finding demonstrates that the viscosity ratio, not the temperature, affects irreducible water saturation (Kumar & Inouye, 1994). Following that, a mathematical model for demonstrating the temperature dependence of relative permeability in terms of water saturation and irreducible water saturation was proposed. Their findings reveal that when the temperature rises, the relative permeability of water and oil decreases and increases, respectively. If irreducible water saturation increases with temperature, the response of relative permeability can be attributed to temperature (Nakornthap & Evans, 1986). According to another study, the effect of temperature on oil–water relative permeability is yet uncertain due to inconsistent findings. The effect of temperature on the rock-fluid system is determined by how temperature affects wettability, interfacial tension, and pore geometry (Esmaeili et al., 2019). The increase in initial water saturation or irreducible water saturation, combined with an increase in the flood temperature, modifies the existing crossover saturation point between oil–water relative permeability curves. Figure 1 shows a graphical presentation of increasing initial or irreducible water saturation and subsequent modification of the existing wetting state of the reservoir rock. Based on the above research findings, the current study is designed to investigate the effect of temperature on the pH of flood water effluent and the initial water saturation of the sandstone rock. Finally, the study will investigate how temperature influences the wettability of sandstone porous media. Apart from above, the wettability alteration process, which is achieved by the synergistic interaction of nanoparticles (NPs) with low salinity water and surfactants, is a novel method for optimising oil recovery while minimising formation damage (Olayiwola & Dejam, 2020). This study, however, is confined to the effect of temperature on wettability change and does not include this strategic, promising, and economically feasible approach for inducing changes in the wetting characteristics of sandstone reservoir rock. Figure 2 summarises the experimental analysis that has been incorporated into the current work.

Sandpacks were employed in the bulk of well-known past research investigations that looked at relative permeability

Fig. 1 Change of crossover point due to temperature effect on irreducible water saturation, hence on oil–water relative permeability curve

Fig. 2 Flow chart for experimental work

properties at higher temperatures. As a result, the produced data are of limited utility and is only relevant to a single well reservoir. In most previous investigations, low-temperature relative permeability data have been regarded as the low-temperature counterpart to high-temperature relative permeability data. In addition, the initial pH and wetting properties of the sandstone core, which change when there is a salinity contrast between the injected brine and the formation water, were also investigated in the previous research. The current study looks at how temperature affects wettability changes in terms of pH, irreducible water saturation, and clay mineralogy or composition in real porous sandstone rock. Furthermore, the majority of prior research studies did not combine

the investigation of all three factors into a single experimental work. This paper uses sandstone cores with a variety of clay minerals and compositions with an attempt to retain the representative behaviour of the sandstone core. The current work includes a rock mineralogy investigation in genuine sandstone cores, where diverse clay minerals such as quartz, plagioclase feldspar, alkali feldspar, kaolinite, illite, smectite, and chlorite are detected in various ratios. As a result, the research findings on clay's involvement or supporting mechanism in low salinity flooding are more trustworthy and reflective of the real producing mechanism. All these set the current study apart and novel from most of the previous research since the findings in this study focus on the mineral

composition effect and its dominance in wettability change in terms of flood water chemistry as well as petrophysical properties of the rock as a result of alternatively injection of low salinity water on crude oil-rock-brine interaction. The current study used an integrated strategy that takes into account crude oil composition, formation water chemistry, physical parameters, and rock mineralogy to investigate the effect of temperature on the wettability of sandstone porous media. By comparing the initial pH of low salinity water before flooding with the pH of the post flood effluent brine at increasing flooding temperature, the current study takes a novel approach to studying the effect of temperature on the Barail sandstone formation adjacent to the oil-producing porous media of the Upper Assam basin. In addition, a comparison has been drawn between the induced changes in initial irreducible water saturation of the sandstone rock when it was subjected to elevated temperatures of 85 °C and 105 °C from 70 °C.

The experimental analysis of the work first presents the materials and methods that characterise the sandstone rock, reservoir fluid, and the rock mineralogy forming the structural composition. Following this, a series of core flood experiments have been performed with low salinity water at three different reservoir temperatures. After that, the discharge of the core flood effluent was screened to see if the initial pH changed at elevated temperatures of 85 °C and 105 °C. From the core flood study, the irreducible water saturation, or S_{wir} , for each core plug was calculated at three different temperatures: 70 °C, 85 °C, and 105 °C. The current study offers a correlation for the Barail sandstone outcrop formation of the Upper Assam basin based on the results of the core flood analysis, which shows the effect of temperature on irreducible water saturation, which is then linked to variations in the wettability of the sandstone rock. The following section summarises the findings and draws a conclusion emphasising the effect of temperature on wettability alteration by presenting this novel approach of injecting alternately low salinity water at increasing core flood temperatures into real sandstone cores representative of the oil-producing porous media of the Upper Assam

basin, where diverse clay mineralogy is present at different ratios and interacts with the low salinity water at different temperatures.

Materials & methods

Materials

The porous media employed in this study was derived from the Barail outcrop formation, which is located near the producing oil reservoirs of the Upper Assam Basin. Table 1 displays the physical and petrophysical parameters of the outcrop core plug data. The formation water (FW) and crude oil samples used in the study were obtained from oil wells in the Upper Assam Basin, which is nearing the depletion stage of production. The crude oil acquired from the oil-producing porous media of the Upper Assam basin was first centrifuged and then filtered (Piñerez Torrijos et al., 2016). Following this, FW was examined for its ion concentration, and the results are presented in Table 2. In the current study, the units for the ion concentrations were kept at mg/L for sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}). The pH of water flood effluents was tested at reservoir temperatures. Brine water samples were

Table 2 Formation Brine composition and properties

Property	Measured value
Major ionic components	
Na^+ , (mg/L)	1540
K^+ , (mg/L)	10.8
Ca^{++} , (mg/L)	22.5
Mg^{++} , (mg/L)	15.0
Total dissolved solids, (mg/L)	3148
Salinity (ppm)	3100
pH	5.6
μ @ 25 °C	1.18
μ @ 60 °C	0.60

Table 1 Properties of sandstone porous media

Core ID	Diameter, D in	Bulk volume, V_{bulk} cm^3	Porosity*, ϕ %	Perm **, k mD	Grain density, ρ_g g cm^{-3}	Rock type RT
X1	1.5	81.7161	0.1525	89.2	2.67	Sandstone outcrop
X2	1.48	63.26384747	0.1328	91.4	2.65	Sandstone outcrop
X3	1.47	64.60170723	0.1525	95.1	2.67	Sandstone outcrop
X4	1.5	70.68569325	0.1235	87.6	2.68	Sandstone outcrop
X5	1.5	74.10596882	0.1726	96.5	2.66	Sandstone outcrop

Perm**: Permeability, *Porosity measured after cleaning at Soxhlet apparatus using solvents toluene: methanol @ 1:1 and dried at Humidity Control Oven

prepared in the departmental laboratory using reagent grade chemicals such as NaCl (99 per cent purity), KCl (99.5 per cent purity), CaCl_2 (98 per cent purity), and MgCl_2 (98 per cent purity) from Merck Specialist Pvt Ltd, India. Crude oil parameters such as density, g/cc (at 15 °C), viscosity, cP (at 40 °C), specific gravity (at 60°/60°F), API gravity (°API), pour point (°C), asphaltene (per cent w/w), acid no, AN (in mg of KOH/g), and base no, BN (in mg of KOH/g) were estimated at room temperature. The characteristics of crude oil are depicted in Table 3.

Methodology

Rock sample analysis

The core sands were first plugged into core plugs, which were then water-washed prior to cleaning in the Dean–Stark apparatus. A solvent mixture of 50:50 toluene and methanol was employed to clean the core samples. Mild heat was set at 40 °C for the solvent mixture in the Dean–Stark

apparatus and the process continued for about 72 h to completely clean the samples. After cleaning, the sand samples were agitated in an ultrasonic cleaner to remove any surface deposits on them. Following that, the samples were dried and warmed for 72 h in a humidity control oven. Before and after cleaning and drying, the weights of the core plug samples were recorded. The bulk volume of the sandstone rocks was calculated using the physical dimensions of the core plugs. The Helium porosimeter, TPI-219, manufactured by Coretest Systems Inc. in the USA, was used to determine the porosity of each dry core plug. The porosity values of the sandstone rock plugs are shown in Table 1. Figure 3 demonstrates the set-up for measuring the porosity of the core plug samples. The Boyle Law Double Cell method was used to measure the porosity of the sandstone core plug samples. TPI 219 is comprised of a single matrix cup with an outside diameter of 1.5 inches. Billets are placed in the cup. The TPI-219 Helium Porosimeter comes with a total of five billets. Each of the five billets represents five different samples with various volumes, namely volumes A (7.209163 cc), B

Table 3 Crude oil properties

AN (mg KOH/g)	BN (mg/KOH/g)	ρ (g/cm ³)	μ @ 15 °C	Specific gravity	Viscosity, cP (40 °C)	Pour point, °C	Asphaltene, % (w/w)	°API
0.12	1.8	0.8583	0.8732	0.8662	3.5	32	1.12	31.85

Fig. 3 TPI-219 set-up for measurement of porosity

(14.40692 cc), C (21.57046 cc), D (28.86337 cc), and E (43.41468 cc). Each billet has a different length (A: 0.248-inch, B: 0.497-inch, C: 0.744-inch, D: 0.997 inch, and E: 1.498 inch). The billets were employed to alter the length of the core plugs, which were then inserted into the matrix cup to assess the sample porosity. Figure 4 depicts the five billets used in the grain volume measurements of the rock samples. The mineral composition of the sandstone rock was then determined using X-ray diffractograms on rock samples. The mineralogy of rocks is reported in Table 4.

Fig. 4 Billets for adjustment of core plug lengths in the core holder of TPI-219

Table 4 Rock mineralogy in weight percentage (wt.%)

Sample ID	Quartz (Q)	Plagioclase feldspar (PF)	Alkali feldspar (AF)	Kaolinite (K)	Illite (I)	Smectite (S)	Chlorite (Ch)
X1	85.47	2.05	1.66	1.62	5.69	1.87	1.64
X2	70.51	3.2	14.1	4.48	4.51	1.92	1.28
X3	72.9	1.37	3.34	16.72	2.67	1.33	1.67
X4	70.32	1.32	4.83	14.83	4.51	1.61	2.58
X5	67.07	7.31	1.25	14.02	4.87	2.43	3.05

Fig. 5 Core flood set-up for WF

the sleeve of the core holder, which houses the core plugs. The rubber sleeve inserted within the core holder provided a firm grip on the core plugs, guiding the injected fluids only via the core plugs. Furthermore, the overburden pressure keeps the annulus between the inserted rubber sleeve and the core plug from leaking. During the core flooding procedure, a heat source with a thermometer was attached to the core flooding chamber (oven) to maintain the temperature of the core plugs. An electronic screen and a back-pressure regulator (BPR) were connected to the core flood set-up to display the internal temperature of the core holder and the system's outlet pressure. The data for the core flooding process was collected in real-time using the attached computer.

pH of the core flood effluent

In this analysis, the physical and petrophysical properties of the outcrop core plugs belonging to the Barail sandstones of the Upper Assam Basin were measured. The core flooding analysis was carried out at three different temperatures: 70 °C, 85 °C, and 105 °C. The temperature ranges were chosen due to the existence of similar reservoir temperatures in some of the Upper Assam Basin's adjacent producing reservoirs. The core plugs were cleaned and dried first. They were then matured in crude oil before being flooded with synthetic brine with salinities of 3100 ppm and 1000 ppm, respectively. The salinity ranges chosen are comparable to and within the salinity limitations of some of the water flood strategies used in the region. The brine (effluent) from the core was collected in the effluent collector. The volume of effluent accumulated during flooding was monitored and recorded as a function of the pore volume (PV). The pH of the flood effluents was evaluated using water analyser equipment (make: Systronics; Model 371).

Determination of Irreducible water saturation, S_{wir}

In the present work, cleaned, dry sandstone core plugs were placed in the core holder. An overburden pressure of 400 psi was maintained in the experimental analysis. Prior to examination, the core plugs were saturated with brine water using a vacuum pump. The PV and porosity of each core plug were measured using the TPI-219 porosimeter. The absolute permeability of the rock samples was determined using a liquid permeameter. The core samples were then inserted into the core holder, and the entire set-up was placed inside the core flooding oven in a horizontal position. The experimental analysis of core flooding for determination of S_{wir} (irreducible water saturation) was performed at three different temperatures, i.e. 70 °C, 85 °C, and 105 °C for each core plug. Water injection was performed once at a time at the predetermined temperatures for five different core plugs until the desired temperature and pressure were reached

inside the core. Following that, oil was pumped at a rate of 0.5 cc/min into each core plug at three distinct temperatures to calculate the initial water saturation, S_{wi} . Since then, oil injection has continued at the S_{wir} in order to calculate the effective permeability of oil. For each series of experimental analyses, a receiver was positioned beneath the core holder's outlet to collect the flood effluents in a continuous process. Following that, the imbibition process was restarted with a 0.8 cc/min infusion of brine water. During water flooding, the oil production rate versus time was recorded, and the pressure differential across the core was monitored for each core flooding analysis. After the experiment, the receiver containing the effluents was immersed in a water bath to maintain the temperature of the experimental analysis constant. The effluents were kept in the water bath for about a week to completely separate the oil/water for measurements of its recovery. Synthetic brines with salinities of 3100 ppm and 1000 ppm were used for the core flooding analysis.

Experimental results

pH

Figures 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 and 20 present the results of the core flood analysis for determining the pH of the water flood effluents. For each of the core plugs in the current investigation, water flooding was performed at three distinct temperatures.

Temperature effect on Irreducible water saturation, S_{wir}

The findings of the core flooding investigation performed on five different core plugs revealed that increasing flooding temperature increases irreducible water saturation, S_{wir} . The

Fig. 6 pH screening test at 70 °C for sandstone core plug X1

purpose of these flooding experiments was to investigate the effect of temperature on irreducible water saturation, S_{wir} , and the resulting changes in the wetting condition of reservoir rock. Table 5 summarises the experimental results of core flooding analyses at three distinct flooding temperatures: 70 °C, 85 °C, and 105 °C.

Result analysis

Clay mineralogy

In the current analysis, the presence of feldspar in the form of plagioclase ($\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$) and alkali feldspar (KAlSi_3O_8 - $\text{NaAlSi}_3\text{O}_8$) was identified in the sandstone rock formations. In addition, the analyses show the presence of quartz, illite, and kaolinite. The presence of the

aforementioned minerals contributes to the sandstone rock's water wetness (Barclay & Worden, 2000). Furthermore, an asphaltene concentration of 1.12 per cent (w/w) was detected in crude oil samples from the Upper Assam basin (Table 3). Asphaltene has a higher propensity for adsorption on feldspar mineral surfaces. This characteristic opens up the possibility of modifying the wetness in the outcrop core (Ehrenberg et al., 1995). Kaolinite [$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$], is a low-swelling clay, identified in the XRD investigation of the Barail formation. In addition to the minerals listed above, smectite, a swelling clay comprised of 2:1 clay in which one octahedral sheet stays sandwiched between two tetrahedral sheets, was detected in the current study.

The presence of the above minerals favours the sandstone rocks to obtain water wetness from flooding. During the core flooding investigation, the pH of the core flood effluent increased for each core plug with the increasing temperature

Table 5 S_{wir} at 70 °C, 85 °C, and 105 °C

Porous media	Core diameter, D, inch	Water flood temperature, °C	Brine salinity, ppm	Injection rate, cc/min	Porosity, ϕ , fraction	Pore volume, PV, cc	S_{wir} %
X1	1.5	70 °C	1000	0.5	0.1525	12.4617	0.29
	1.5	85 °C	1000	0.5	0.1525	12.4617	0.33
	1.5	105 °C	1000	0.5	0.1525	12.4617	0.34
	1.5	70 °C	3100	0.5	0.1525	12.4617	0.27
	1.5	85 °C	3100	0.5	0.1525	12.4617	0.31
	1.5	105 °C	3100	0.5	0.1525	12.4617	0.32
X2	1.48	70 °C	1000	0.8	0.1328	8.4014	0.26
	1.48	85 °C	1000	0.8	0.1328	8.4014	0.31
	1.48	105 °C	1000	0.8	0.1328	8.4014	0.32
	1.48	70 °C	3100	0.8	0.1328	8.4014	0.26
	1.48	85 °C	3100	0.8	0.1328	8.4014	0.33
	1.48	105 °C	3100	0.8	0.1328	8.4014	0.34
X3	1.47	70 °C	1000	1	0.1525	9.8518	0.3
	1.47	85 °C	1000	1	0.1525	9.8518	0.33
	1.47	105 °C	1000	1	0.1525	9.8518	0.33
	1.47	70 °C	3100	1	0.1525	9.8518	0.29
	1.47	85 °C	3100	1	0.1525	9.8518	0.32
	1.47	105 °C	3100	1	0.1525	9.8518	0.33
X4	1.5	70 °C	1000	0.5	0.1235	8.7297	0.29
	1.5	85 °C	1000	0.5	0.1235	8.7297	0.32
	1.5	105 °C	1000	0.5	0.1235	8.7297	0.33
	1.5	70 °C	3100	0.5	0.1235	8.7297	0.28
	1.5	85 °C	3100	0.5	0.1235	8.7297	0.32
	1.5	105 °C	3100	0.5	0.1235	8.7297	0.33
X5	1.5	70 °C	1000	1	0.1726	12.7907	0.31
	1.5	85 °C	1000	1	0.1726	12.7907	0.33
	1.5	105 °C	1000	1	0.1726	12.7907	0.33
	1.5	70 °C	3100	1	0.1726	12.7907	0.3
	1.5	85 °C	3100	1	0.1726	12.7907	0.33
	1.5	105 °C	3100	1	0.1726	12.7907	0.33

of the core flood experiments. Furthermore, the salinity of the injected water was low in this study. As a result, it contributes to the water wettability of the outcrop rock (Barclay & Worden, 2000). Furthermore, in the current investigation, the occurrence of kaolinite in certain outcrop samples was found to be greater than 10% by weight (wt%). As the pH of flood water rises, so does the adsorption of polar components onto kaolinite clay. However, decreases in salinity have no substantial influence on adsorption (Puntervold et al., 2018). The water wetness in some porous media will be lower as a result of this feature. Taking everything into account, this study concludes that the Barail sandstone outcrop formation possesses characteristics that contribute to sandstone rock mixed water wetness.

pH determination

Core X1

In the first analysis, the sandstone rock plug X1 was subjected to brine water flooding with 3100 ppm and 1000 ppm NaCl solutions. The first batch of brine floods was performed at a core temperature of 70 °C using a 3100 ppm NaCl solution. The initial brine effluent pH was 7.1, and the pH was reduced to 6.8 following 1.5 PV injection with 3100 ppm NaCl solution. Following that, when brine flooding of 1000 ppm NaCl solution was performed on the same core at 1.5 PV of injection, pH increased to a stabilised pH of 9.4. (Fig. 6). The pH gradient increased by around 2.3 after 1000 ppm brine water flooding was performed at a reservoir temperature of 70 °C. When flooded with the 3100 ppm NaCl solution (3PV), the pH of the brine effluent dropped once more. After that, it gradually increased from a pH of 6.9 to 7.01 in response to the 3.8 PV injection of the X1 core.

The initial pH was stable at 7.2 for 1 PV of injection in the second core flood with 3100 ppm NaCl solution at a pre-determined core temperature of 85 °C. (Fig. 7). After that, a 1.5 PV injection (4–5.5 PV) resulted in a pH of 6.8. The pH increased to 9.4 after brine intervention into the core with a 1000 ppm NaCl solution (Fig. 7). During the successive flooding at 1000 ppm, a smooth, incremental pH gradient of roughly 2.2 was achieved. When the third batch of flooding with 3100 ppm NaCl solution resumed after 5.5–7 PV of 1000 ppm brine water injection, the pH value decreased to 6.9. (Fig. 7). The initial pH was recorded to be 6.8 during the third successive flood (3100 ppm) at 105 °C before stabilising at 8.4 for the second batch of floods with 1000 ppm NaCl solution. When moving from 1000 ppm brine flooding to 3100 ppm brine flooding, the pH dropped quickly and eventually stabilised at 7.02. (Fig. 8).

The above findings showed an added pH value of 2.2–2.3 at flooding temperatures of 70 °C and 85 °C due

Fig. 7 pH screening test at 85 °C for sandstone core plug X1

Fig. 8 pH screening test at 105 °C for sandstone core plug X1

to 1000 ppm brine water flooding. The rise in pH indicates that the outcrop cores may have reached alkaline conditions. When the pH increases to alkalinity, the adsorption of organic molecules by feldspar and other clay minerals is reduced (Mamonov et al., 2017). However, increasing flooding temperatures, particularly above 100 °C, were observed as the cause of reduced pH during water flooding in the current study. When flooded at 105 °C, the pH of the 1000 ppm brine flood effluent dropped to 8.4 (Fig. 8). The pH of the flood effluent with 1000 ppm NaCl solution was 9.4 when core flooding was performed at a temperature of 85 °C (Fig. 7). Based on the above, it is worth noting that the pH of the water flood effluent will continue to fall as flood temperatures rise, particularly above 100 °C. Because the kaolinite content of the core X1 is lower than that of the feldspar, core flooding with increased flooding temperatures may alter the wettability of the sandstone rock. Nonetheless, the current study demonstrated that brine flooding of sandstone rock with a 1000 ppm salinity solution increased

the pH of the flood effluents by 2–3 units higher than the pH reached with the 3100 ppm NaCl solution as temperature increased.

Core X2

Figures 9, 10, and 11 show the results of the pH of the core flood effluents. The flooding experiment was conducted on sandstone core plug X2 at set temperatures of 70 °C, 85 °C, and 105 °C. In the analysis, the sandstone core was flooded in batches. The brine flooding with 3100 ppm NaCl solution resulted in a pH of 6.9 for the first batch of core floods done at the predetermined sandstone core temperature of 70 °C. The pH increased to 9.6 during the subsequent brine flooding (second batch, 1000 ppm) (Fig. 9). When the flooding sequence was changed from 3100 ppm salinity to 1000 ppm solution, the pH gradient increased by around 2.7. (Fig. 9). When the 1000 ppm brine flood was halted and 3100 ppm NaCl solution flooding resumed, the pH decreased to 7.1.

The initial pH registered as 7.1 in the second experimental examination, with the first batch of flooding with salinity of 3100 ppm NaCl solution at an enhanced temperature of 85 °C. This pH value at 85 °C was 0.2 units higher than the previous batch of floodwaters at 70 °C (Fig. 10). By switching to brine flooding with a 1000 ppm solution at the stipulated core temperature of 85 °C, the pH of the brine effluent was increased to 9.7. This is a 2.6 pH gradient increase recorded after flooding the 4.4 PV of the core plug (Fig. 10). When the brine was flooded with 3100 ppm solution again, the pH dropped to its original value of 7.1.

Similarly, the initial pH was 6.9 in the first batch of the third cycle of the core flood experimental study, with the flooding temperature set at 105 °C. Flooding with 1000 ppm solution elevated the pH by 8.7, which was less than the pH observed at core temperatures of 70 °C and 85 °C. (Fig. 11).

Fig. 10 pH screening test at 85 °C for sandstone core plug X2

According to the results of the preceding investigation, the first cycle of successive floods at 70 °C resulted in an initial pH value of 6.9 for 3100 ppm brine flooding (Fig. 9). The low pH gradient of 1.9 was obtained with 1000 ppm brine flooding during the third cycle of flooding at 105 °C. Furthermore, the change in the wettability of the sandstone core is demonstrated by the rise in the pH gradient upon flooding with 1000 ppm brine solution at increasing flooding temperatures from 70 to 85 °C. The second flood, at 85 °C, resulted in an increase in the pH of the flood effluents for the sandstone core plug X2. This rise could be related to the presence of feldspar (14.1 weight per cent) in the sandstone reservoir. Feldspar can transform the initial wettability of sandstone rock towards higher water wetness by adjusting pH and increasing reservoir temperature.

Fig. 9 pH screening test at 70 °C for sandstone core plug X2

Fig. 11 pH screening test at 105 °C for sandstone core plug X2

Core X3

The results of the pH screening test for the sandstone outcrop core X3 at core flood temperatures of 70 °C, 85 °C, and 105 °C are shown in Figs. 12, 13, and 14. The first batch of floods produced a pH of 7.2 at a core temperature of 70 °C. The pH initially decreased to 6.7 at the start of the core flood, but eventually stabilised at 7.2 after 0.5 PV (pore volume) of the first batch of injection (Fig. 12). The pH of the brine flood effluent increased dramatically from 7.2 to 9.6 when the flooding was changed from the first batch (3100 ppm) to the second batch (1000 ppm). The second batch of floods indicated an incremental pH gradient of about 2.4. Similarly, when the flood sequence was restored to the third batch of 3100 ppm flooding, its pH dropped to 7.2. (Fig. 12).

The core plug was then subjected to the second flood cycle of examination at a higher temperature of 15° C than the first flood cycle. The pH of the first batch of floods with a 3100 ppm NaCl solution was 7.2. (Fig. 13). For the second batch of floods with 1000 ppm solution at 85 °C, an incremental pH gradient of 2.5 was recorded, which is 0.1 unit higher than the pH achieved for the 70 °C flood. When the floods were switched from the second to the third batch (Fig. 13), the pH value declined from 9.7 to 7.2 for the sandstone porous media with a 16.72 weight per cent of kaolinite clay. The first batch of injections in the last flood at 105 °C resulted in a pH of 6.8, which was 0.4 unit lower than the pH recorded for reservoir temperatures of 70 °C and 85 °C (Fig. 14). Furthermore, switching from the first batch (105 °C, 3100 ppm) to the second batch (1000 ppm) resulted in a rise in pH to 9.8. (Fig. 14). The investigation shows that the outcrop core, X3, with a 16.72 weight % of kaolinite clay, resulted in a rising pH gradient as core flood temperatures increased. However, when the injected flood was in the third batch, the pH dropped rapidly (3100 ppm

Fig. 13 pH screening test at 85 °C for sandstone core plug X3

solution). After 6PV of injection, the pH of the third flood finally stabilised at 7.2.

According to the aforementioned analysis of core flooding of the sandstone core X3 at temperatures of 70 °C, 85 °C, and 105 °C, brine flooding of 1000 ppm salinity resulted in growing pH gradients with increasing temperature. This could be related to the changes in the wettability of sandstone rock surfaces due to the presence of kaolinite in a significant weight per cent (16.72 wt.%) than other minerals (Piñerez et al. 2016).

Core X4 and X5

Core plugs DG4 and DG5 with kaolinite weight percentages of 14.83 (wt%) and 14.02 (wt%) were examined in this study. The pH of brine effluents was measured at temperatures of 70 °C, 85 °C, and 105 °C. The results of the analysis, as shown in Figs. 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 and 20, established that pH gradients

Fig. 12 pH screening test at 70 °C for sandstone core plug X3

Fig. 14 pH screening test at 105 °C for sandstone core plug X3

Fig. 15 pH screening test at 70 °C for sandstone core plug X4

Fig. 18 pH screening test at 70 °C for sandstone core plug X5

Fig. 16 pH screening test at 85 °C for sandstone core plug X4

Fig. 19 pH screening test at 85 °C for sandstone core plug X5

Fig. 17 pH screening test at 105 °C for sandstone core plug X4

Fig. 20 pH screening test at 105 °C for sandstone core plug X5

increased during brine flooding with 1000 ppm NaCl solution at temperatures of 70 °C, 85 °C, and 105 °C. An incremental pressure gradient of 2.3 (Fig. 15) at 70 °C, 2.4 (Fig. 16) at 85 °C, and 2.46 (Fig. 17) at 105 °C resulted in the second batch of brine flooding of outcrop core X4. Similarly, during the second batch of brine water flooding, the incremental pressure gradient in X5 was in the range of 2.1 (Fig. 18) in the first flood at 70 °C, 2.3 (Fig. 19) in the second flood (1000 ppm) at 85 °C, and 2.26 (Fig. 20) in the third flood at 105 °C.

Based on the results of the above investigation for cores X1 to X5, it is found that brine water flooding induces a greater pH of flood effluents with increasing flooding temperature. It has also been observed that cores with higher kaolinite weight percentages create higher pH when core flood temperature increases.

Effect of temperature on irreducible water saturation, S_{wir}

X1

By flooding the cores at three distinct temperatures: 70 °C, 85 °C, and 105 °C, the current study investigated the effect of temperature on irreducible water saturation, S_{wi} . When the core plug X1 was flooded with brine water (NaCl: 1000 ppm) at a temperature of 70 °C, the irreducible water saturation (S_{wir} or S_{wi}) was found to be 0.29. However, as the flooding temperature increased from 85 to 105 °C, the irreducible water saturation, S_{wir} , increased to 0.33 and 0.34, respectively. The results in Table 5 for porous material X1 demonstrate that the initial or irreducible water saturation (S_{wi}) increases with increasing temperature. Furthermore, core flooding the sandstone porous media with a 3100-ppm salinity NaCl solution at a core temperature of 70 °C resulted in an initial or irreducible water saturation (S_{wir}) of 0.27. The irreducible water saturation (S_{wir}) increased to 0.31 and 0.32 when flooded with 3100 ppm NaCl solution at core temperatures of 85 °C and 105 °C, respectively.

According to the results of the core flooding on X1, the irreducible water saturation of the core plug increased with increasing core flood temperature. This increased initial water saturation (S_{wi}) or irreducible water saturation (S_{wir}) behaviour for the core plug X1 at elevated temperatures (85 °C to 105 °C) is consistent with Hamouda and Karoussi's experimental work (2008) (Hamouda & Karoussi, 2008). Furthermore, it is obvious that increasing the temperature of the core flood will affect the crossover saturation point of the relative permeability curve between oil and water. This behaviour depicts how water wetness increases at high temperatures (Hamouda et al., 2008).

X2

After a core flood investigation utilising a 1000 ppm brine solution on the sandstone core plug X2 at a core flood temperature of 70 °C, the irreducible water saturation (S_{wir}) was 0.26. When flooded at temperatures of 85 °C and 105 °C, the irreducible water saturation (S_{wir}) increased to 0.31 and 0.32, respectively. This finding on X2 may be related to Poston et al. (1970) and Sinnokrot's (1971) observations that increasing core flood temperature increases irreducible water saturation (S_{wir}) of the sandstone porous rock (Poston et al., 1970) (Sinnokrot et al., 1971). Further investigation into the effect of temperature on irreducible water saturation using 3100 ppm NaCl solution revealed that the irreducible water saturation was 0.26 at a flood temperature of 70 °C, increased to 0.33 and 0.34 when determined at relatively higher temperatures of 85 °C and 105 °C.

The abovementioned patterns of increasing irreducible water saturation S_{wir} with increasing core temperature, T , would indicate a positive slope of the ratio of dS_{wi}/dT (Hamouda & Karoussi, 2008) (Nakornthap & Evans, 1986). Furthermore, the increase in irreducible water saturation, S_{wir} , with brine flooding at increasing core flooding temperatures implies that the crossover points of the oil and water relative permeability curves have shifted from their initial value of 0.26 as found at the core flood temperature of 70 °C. Based on the above findings and taking into account sand rock mineralogy studies, it is possible to assume that the presence of feldspar and kaolinite in X2 will affect the wettability of the sandstone rock during water flooding (Kim & Lee, 2017).

X3

The core flooding of the sandstone rock plug, X3, with a 1000 ppm NaCl brine solution at 70 °C resulted in an irreducible water saturation, S_{wir} , of 0.3. Following that, for both experimental studies done at increasing core temperatures of 85 °C and 105 °C, the irreducible water saturation, S_{wir} , increased to 0.33. The brine flooding with a 3100 ppm NaCl solution resulted in an irreducible water saturation, S_{wir} of 0.29 for the sandstone core against a core (reservoir) temperature of 70 °C, which increased to 0.32 and 0.33 with flooding temperatures of 85 °C and 105 °C, respectively.

Based on the data above, it can be seen that as the flooding temperature is increased to 85 °C and 105 °C, the intersection point for the oil and water relative permeability curves will also progress due to increasing S_{wir} with flood temperature. Furthermore, the high kaolinite content in sandstone porous media causes the crude oil-rock-brine interaction to increase irreducible water saturation and hence alters reservoir rock wettability as reservoir temperature increases (Kim & Lee, 2017).

Fig. 21 Effect of temperature on S_{wir} for X1 (brine salinity: 1000 ppm)

Fig. 22 Effect of temperature on S_{wir} for X1 (brine salinity: 3100 ppm)

X4 and X5

The results of the temperature effect on irreducible water saturation, S_{wir} , for sandstone core plugs X4 and X5 were found to be similar to the results obtained for sandstone core plugs X1, X2, and X3. The experimental results of X4 and X5 indicated that irreducible water saturation (S_{wir}) and hence water wetness of the sandstone rock plugs increased when the core flood temperature increased from 70 °C to 85 °C and 105 °C. In the core flood investigation of X4 with salinities of 1000 ppm and 3100 ppm NaCl solutions, the irreducible water saturation, S_{wir} , was 0.29 and 0.28 at a core temperature of 70 °C. Following that, when flood temperatures reached 85 °C and 105 °C, the irreducible water saturation increased to 0.32 and 0.33, respectively. Similarly, the irreducible water saturation, S_{wir} , for the outcrop core X5, was determined to be 0.31 and 0.30 for core flood temperatures of 70 °C. Following that, brine flooding with 1000 ppm and 3100 ppm NaCl solutions at escalating temperatures of 85 °C and 105 °C increased S_{wir} to 0.33 in all cases.

The above pattern of increasing irreducible water saturation, S_{wir} , of sandstone rock with increasing temperature for the core plugs X4 and X5, determined in the current investigation, is similar to Kim and Lee's findings (2017).

Correlation of irreducible water saturation, S_{wir} with flood temperature

Table 5 shows the trend of increasing initial or irreducible water saturation, S_{wir} , as core flood temperature increases for core plugs X1, X2, X3, as well as X4, and X5. After core flooding multiple sandstone core plug samples, a linear link was found between S_{wir} and water flood temperatures of 70 °C, 85 °C, and 105 °C. Temperature-induced S_{wir} variation patterns are depicted in Figs. 21 and 22 for the X1 plug

Fig. 23 Effect of temperature on S_{wir} for X2 (brine salinity: 1000 ppm)

Fig. 24 Effect of temperature on S_{wir} for X2 (brine salinity: 3100 ppm)

Fig. 25 Effect of temperature on S_{wir} for X3 (brine salinity: 1000 ppm)

Fig. 28 Effect of temperature on S_{wir} for X4 (brine salinity: 3100 ppm)

Fig. 26 Effect of temperature on S_{wir} for X3 (brine salinity: 3100 ppm)

Fig. 29 Effect of temperature on S_{wir} for X5 (brine salinity: 1000 ppm)

Fig. 27 Effect of temperature on S_{wir} for X4 (brine salinity: 1000 ppm)

Fig. 30 Effect of temperature on S_{wir} for X5 (brine salinity: 3100 ppm)

Table 6 Correlation of S_{wir} vs flood temperature

Porous media (Core plug)	Brine salinity, ppm	Proposed correlation (T vs S_{wir}) (linear)	Relative correlation (T vs S_{wir}) (linear)
X1	1000	$S_{wir} = 0.00025 T + 0.27$	$S_{wir} = 0.000225 T + 0.26755$
	3100	$S_{wir} = 0.00025 T + 0.25$	
X2	1000	$S_{wir} = 0.0003 T + 0.2367$	
	3100	$S_{wir} = 0.0004 T + 0.23$	
X3	1000	$S_{wir} = 0.00015 T + 0.29$	
	3100	$S_{wir} = 0.0002 T + 0.2733$	
X4	1000	$S_{wir} = 0.0002 T + 0.2733$	
	3100	$S_{wir} = 0.00025 T + 0.26$	
X5	1000	$S_{wir} = 0.0001 T + 0.3033$	
	3100	$S_{wir} = 0.00015 T + 0.29$	

sample, Figs. 23 and 24 for X2, Figs. 25 and 26 for X3, Figs. 27 and 28 for X4, and Figs. 29 and 30 for X6. Based on examinations of the S_{wir} trend for each core plug, the current work provides a linear correlation for measuring S_{wir} as a function of temperature, and is presented in Table 6.

Summary and conclusions

This study compared the initial pH of the low salinity water before injection into the sandstone porous media with the pH of the post-water flooding effluent from the cores at elevated temperatures of 85 °C and 105 °C above 70 °C. This is a novel strategy in examining the alteration of the wetting properties of sandstone rock in terms of the changes in the pH of the flood water from its effluent from the sandstone cores. With respect to the Barail formation, the current experiment on sandstone core employed alternate injections of low salinity water at increasing temperatures. This novel approach combines the influences of temperature, rock mineralogy, irreducible water saturation, and sandstone rock response to achieve alkaline behaviour during crude oil-rock-water interaction. This strategy of altering wettability towards water wetness by injecting low salinity water is advantageous and beneficial to the oil industry because it is less expensive and does not damage the formation. Furthermore, because this method promotes wettability change in sandstone rock towards water wetness, the data obtained with this method might be utilised as a reference for showing the temperature dependence in wettability alteration of sandstone rock. By analysing the pH of the post-water flood effluents, the results of the core flood study also reveal whether the surface of sandstone rock is acidic or basic. The current study presents a method for analysing the wettability alteration impact of irreducible water saturation at elevated core flooding temperatures, and thus provides indirect information about wettability behaviour. Despite the fact that there is no consensus among scholars on the link between relative

permeability effects and the wettability change process, the current study indicates temperature dependency behaviour in the Upper Assam basin's Barail formation. However, further research will be done in this area to evaluate the process of wettability alteration in sandstone rock utilising the approach of measuring contact angle rather than analysing the relative permeability effects. This future work will help eliminate the disadvantage of not having consensus regarding the temperature effect on the wettability behaviour of sandstone rock surfaces through investigation of the oil–water relative permeability behaviour.

Further, this paper discusses the impact of rock mineralogy as an integrated effect of different clay minerals found in the Barail sandstone rock. Unlike most other research, the current study did not use synthetic mineralogical columns representing individual clay minerals to decode or quantify the role of individual clay minerals in the effect of temperature on wettability change and, as a result, on oil recovery. As such, the investigation of the impact of specific clay minerals on the wettability alteration process as a result of low salinity water flooding at high temperatures is limited as a result of this limitation. Also, the time it takes for sandstone rock to respond to changes in wetting conditions varies based on the reservoir rock's petrophysical properties. Many recent studies have revealed that sequential alternate injection of nanoparticles (NPs) with low salinity water and surfactant solution is another promising innovative technique for dealing with wettability change in sandstone reservoir rock that does not cause formation damage (Olayiwola & Dejam, 2020).

Based on the findings of the XRD study, as well as the core flood examination of the sandstone rock to examine the effects of temperature on irreducible water saturation and pH of the water flood effluents, the current work derives the following conclusions:

1. Increasing flooding temperatures cause an increase in the pH of the core flood effluent. However, pH drops when the reservoir temperature is 105 °C for the current study.

2. The current study finds that with increasing temperature, the irreducible water saturation, S_{wir} increases linearly. This increased S_{wir} shifts the position of the crossover saturation point, indicating the possibility of changing wettability in the sandstone rock (Zhang et al., 2017).

3. According to the findings of the core flood investigation, increasing reservoir temperature shifts the crossover point saturation to the right, facilitating the attainment of water wettability in the sandstone rock. The reservoir clay mineralogy has a significant impact on the wettability of the sandstone rock during water flooding.

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