Optimizing Ion-Tuned Diluted Formation Water for Sustainable Enhanced Oil Recovery in Sandstone Reservoir

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Abstract
Ion-tuned diluted formation water (DFW) optimization offers a sustainable alternative to conventional low-salinity water (LSW) flooding for enhanced oil recovery (EOR) in sandstone reservoirs. This study investigates the effects of DFW and LSW through wettability alteration (WA), zeta potential (ZP), conductivity measurements, X-ray diffraction (XRD), Scanning electron microscopy (SEM) and coreflooding experiments. DFW samples were prepared by diluting distilled water (DW) in ratios of 1:1 to 1:9, with DFW-7 exhibiting properties closest to LSW and selected for further comparison. Experimental results demonstrate that ion-tuned dilution effectively modifies rock-fluid interactions, reducing clay swelling and enhancing oil displacement.

ZP measurements indicated increased electrostatic stability, while conductivity trends confirmed reduced salinity, minimizing formation damage. XRD and SEM analyses showed that DFW-7 mitigates pore-scale mineral precipitation and clay swelling, preserving permeability better than LSW. Coreflooding confirmed DFW-7 recovered 56.41% IOIP while maintaining reservoir integrity whereas LSW achieved higher initial recovery (61.44% IOIP) but led to greater permeability loss due to fines migration. LSW improves wettability alteration and recovery efficiency, it risks long-term reservoir damage. DFW-7 offers an optimal balance between formation stability and EOR efficiency, making it a more sustainable and field-applicable technique for sandstone reservoirs.

Keywords: Low Salinity Water Flooding, Contact Angle, Wettability Alternation, Zeta Potential, Electrical Double Layer, Enhanced Oil Recovery, Diluted Formation Water.

Introduction

Over the past few decades, low salinity waterflooding (LSWF) has gained widespread acceptance as a significant enhanced oil recovery (EOR) technique because of its remarkable contribution to the petroleum industry in terms of enhancing oil displacement efficiency[10,22,33]. Several laboratory studies have demonstrated that increased recovery of oil from sandstone reservoirs can be achieved by modifying the composition and salinity of injected brine[2,11,14,22,23,30]. However, recent advancements have suggested that ion tuned diluted formation water (DFW) represents an advanced evolution of LSWF, offering more controlled and optimized oil recovery mechanism. LSWF improves oil recovery by altering rock-fluid interactions, ion tuned DFW selectively adjusts specific ions thereby optimizing wettability alteration, interfacial tension and ionic exchange[4,14]. This controlled dilution of formation water mitigates the flaws associated with conventional LSWF such as clay swelling, fines migration and unpredictable pH variations[29], ensuring improved sweep efficiency and reservoir compatibility[22 27]. In other words, diluting and tuning the composition of the formation brine is an improved oil recovery technique that enhances oil recovery compared to conventional waterflooding/ LSW method[1,2,22,23].

Unlike conventional waterflooding or LSWF, there are certain advantages of DFW which makes it a more sustainable approach for maximizing hydrocarbon recovery. Some of the benefits can be summarised as:
(i) use of DFW minimizes the reliability of waterflooding experiment on external freshwater sources,
(ii) it lowers the risk of disposing high salinity produced water by modifying and recycling the formation water composition itself,
(iii) DFW lowers operational costs by altering wettability of the rock surface naturally thereby reducing use of chemical additives,
(iv) use of diluted brine reduces scaling effect in pipelines and reservoirs thereby extending the life of the equipment,
(v) DFW reduces carbon emissions by minimizing energy intensive water treatment operations, freshwater transportation. With continued field trials and researches, DFW is believed to optimize oil recovery thereby reducing the negative impacts of conventional LSWF technique.

The effectiveness of DFW can be explained through the proposed mechanisms of LSWF. Bernard[6] demonstrated that improved oil recovery in sandstones cores is attributed to fines migration and clay swelling upon freshwater injection.

Later Tang and Morrow[27] revealed that stripping off the mixed wet particles from pore spaces shifts wettability causing recovery. The selective adjustment of ions in injection water modifies the wettability of the rock surface by exchanging ions between injected water and rock surface thereby improving crude oil-brine interactions leading to incremental oil recover[14]. In general researchers agree that tuning and dilution of injection water affect reservoir wettability to become water wet, improving recovery[4,23].

The initial wetting properties of reservoir rock is related to the presence of polar components in crude oil. Ligthelm et al[16] suggested that the shift in wettability is caused by electrical repulsion of polar oil components from rock surface that expands the electrical double layer around the rock surface. The injection of diluted water into reservoir preferentially triggers the electrical charges at rock/brine and oil/brine interfaces thereby improving oil recovery[19,32]. In addition to this, previous researches have documented that the magnitude of change in electrical charges at rock/brine and oil/brine interfaces is pH dependent[19,32].

The main objective of this study is to evaluate and to compare the effectiveness of DFW (Diluted Formation Water) and conventional LSW (Low Salinity Water) in enhancing oil recovery by examining the impact of ionic strength, pH variations and conductivity changes on recovery efficiency. Additionally, the study aims to adopt DFW as a comprehensive approach to maximize recovery while ensuring the long-term sustainability of reservoir performance.

Material and Methods

Crude Oil (CO) and formation water (FW): The CO and FW were collected from oil and gas fields of Oil India Limited. The properties of the crude oil used in this study are tabulated in table 1. FW was diluted by distilled water (DW) in ratio 1:1, 1:3, 1:5, 1:7, 1:9 for comparison analysis.

Table 1
Properties of crude oil

Property	CO
Sp. gravity of crude oil @ 60ºF	0.912
Acid no. of crude oil, mg KOH/g	0.21
Wax content, % (w/w)	2
Asphaltene content, % (w/w)	4.59
Resin content, % (w/w)	9.78
Pour point, ºC	15º

Reservoir Rock (RR): The RR was also collected from oil and gas fields of Oil India Limited. The collected RR was from depth of range 3050.86 – 3051.00 m. XRD and SEM experiments were conducted to identify the dominated clay and to know the significance of clay with EOR. The core plugs of dimensions 3.80 cm length and 5.76 cm diameter were prepared for coreflooding experiment, core disk dimensions 3.80 cm in diameter and 1 cm length prepared for wettability tests and few grams of powder was prepared with help of mortar for sieve analysis to SEM and XRD analysis.

Physical and Chemical properties of water samples: The physical properties salinity, TDS, pH, conductivity and turbidity were determined by the water analyzer. Other physical properties like hardness and alkalinity (HCO_3^-), chloride (Cl^-) and sulphate (SO_4^{2-}) were determined by titration process. Oil and grease (O and G) were determined by the separation process. The ions Na, K and Ca were determined by Flame Photometer. Mg was determined by ICP-OES.

SEM and XRD: After sieving, the powder was separated into 2-3 grams for SEM analysis and a few grams for the pipetting process for XRD study. The fine sand powder from the PAN was poured in one-litter DW in the measurement cylinder using the pipetting technique. Following five to ten minutes of thorough agitation with a magnetic stirrer, the liquid was left undisturbed for an hour. A pipette of the solution supernant containing five millilitres was placed into a small beaker. Since clay minerals are lighter than other minerals, the supernatant was extracted from the top of the solution level.

Wettability Alternation measurement: The sessile drop method, which calculates the angle between a liquid and a rock surface, was used to estimate the CA. Following a thorough cleaning in a Soxhlet extraction system and drying in an oven set at 60°C the reservoir core plugs were sliced into cylindrical core discs measuring 3.80 cm in diameter and 0.70 cm in thickness. The core disc was saturated first in synthetic formation brine and then in crude oil for a period of 7 days at reservoir temperature of 75°C each. A Hamilton microsyringe, model 1005 LTR SYR, was then used to drop 100 µL of an aqueous solution onto the core disc and let it equilibrate for 10 minutes to determine the CA. Using a Dino-lite microscope and the image analysis software displayed, snapshot of the angle created by the drop was captured.

ZP measurement: The ZetaPALS (Phase Analysis Light-Scattering) technique was used to measure the Zeta potential of oil/brine and rock/brine interfaces. This instrument uses He/Ne laser as a light source to measure the electrophoretic mobility of charged particles. The pH of the solutions was adjusted as per requirement. Each of the solution was mixed by an agitator for 2 hrs and then transferred to a cuvette to run the Zeta potential measurements. Three runs were conducted for each sample and the average was taken.

Conductivity and pH measurement: The conductivity and pH of the prepared samples were tested in the water analyser instrument. The conductivity measurement can be evaluated with the swelling reservoir clay minerals with variation of pH by concentrations of NaOH.

Coreflooding experiment: Flooding experiment conducted Hassler core holder of the core flood apparatus shown in figure 1. Equations 1 to 5 are used to find out flooding results. The pore volume (PV) of core plug can be determined by following equations:

$$PV = \frac{\Pi}{4} D^2 L \times \Phi \qquad (1)$$

$S_{oi} = \frac{Brine flushout - LV}{PV}$ (2)

$$S_{wc} = \frac{PV - S_{oi}}{PV}$$ (3)

$S_{or} = \frac{Soi - oil flushout}{PV}$ X 100 % (4)

$R_{Sor} = \frac{oil\ recover\ by\ final\ slug}{volume\ of\ initial\ oil}$ X 100 % (5)

Results and Discussion

Physical and Chemical properties of water samples: Table1 showed the physical and chemical properties of FW and effects of the properties diluted by DW and changes comparison with LSW (5000 ppm NaCl). There were four diluted FW samples prepared namely DFW-3, DFW-5, DFW-7 and DFW-9 diluted by DW of dilution factor (DF) 30 %, 50 %, 70 % and 90%. The results found that when dilution increases, physical and chemical properties decreased. As salinity decreases, conductivity decreases as well. This occurs because the concentration of dissolved salts (such NaCl, KCl, Mg_2SO_4 etc.) in water is represented by salinity and these salts separate into ions (like Na^+ and Cl^-).

More dissolved salts result in increased ionic concentration, which raises conductivity because electrical conductivity (EC) is dependent on the presence of free ions that have the capacity to transport an electrical charge[1]. Sand particles, silt and oil droplets are examples of suspended particles that create turbidity. Turbidity is decreased when these particles are diluted because their concentration per unit volume drops. TDS stands for dissolved minerals and salts. A lower TDS value results from dilution, which lowers their concentration[19,24]. The pH has variable effect. The exact effect depends on the initial pH of the FW. Dilution with neutral DW (~pH 7) will bring the FW's pH closer to neutrality if it is very acidic or alkaline. The FW starting pH determines the precise impact[1]. The O and G is hydrophobic in nature and it may exist as emulsions.

Although dilution lowers their concentration, additional separation techniques could be needed for total removal. The sample DFW-7 with 70% dilution showed near values of parameters with LSW. Therefore, LSW and DFW-7 were considered for coreflooding to understand between better recovery.

Figure 1: Coreflooding Apparatus

Table 2
Physical and Chemical properties of FW, DFW and LSW

S.N.	Parameters	FW	DFW-3 (30%)	DFW-5 (50%)	DFW-7 (70%)	DFW-9 (90%)	LSW (5000 ppm NaCl)
1	pH	8.4	7.89	7.21	6.73	6.15	6.8
2	Salinity (ppm)	14,770	11,770	9654	5312	1900	5,000
3	TDS (ppt)	15.12	11.11	8.67	5.11	3.59	4.87
4	Turbidity (NTU)	113	82	34	12	3	0
5	Conductivity (mS)	11.6	8.98	7.05	4.19	1.77	5.2
6	Na (ppm)	52100	12901	7290	2542	901	1907
7	K (ppm)	3711	1956	1321	987	209	0
8	Ca (ppm)	10791	8763	5432	3123	555	0
9	Mg (ppm)	1790	1321	876	432	21	0
10	HCO_3^- (ppm)	220	154	109	56	21	0
11	SO_4^{2-}(ppm)	410	290	145	57	7	0
12	Cl^- (mg/L)	161000	99078	22121	3987	1121	3111
13	O & G (mg/L)	2700	2213	1321	671	298	0

*DFW-3, DFW-5, DFW-7 & DFW-9 stands for 30%, 50 %, 70 % and 90 % diluted by DW & LSW stands for 5000 ppm NaCl.

SEM and XRD: XRD and SEM reveal the presence of kaolinite and illite in the reservoir rock with higher quantities of quartz. The mineralogy of reservoir rock is shown in table 3, with the microphotographs of kaolinite, illite and quartz obtained from SEM.

Wettability Alteration (WA): The effectiveness of oil recovery, especially in sandstone reservoirs, is greatly influenced by wettability. To improve oil displacement in enhanced oil recovery (EOR), wettability can be altered by diluting formation water with distilled water, which will make it more water wet.

Table 3
Mineralogy of Sandstone RR

Minerals	Amount (%)
Quartz	44.9
Kaolinite	16.6
Illite	15.7
Chlorite	8.9
Albite	8.3
Calcite	5.3
Montmorillonite	0.3

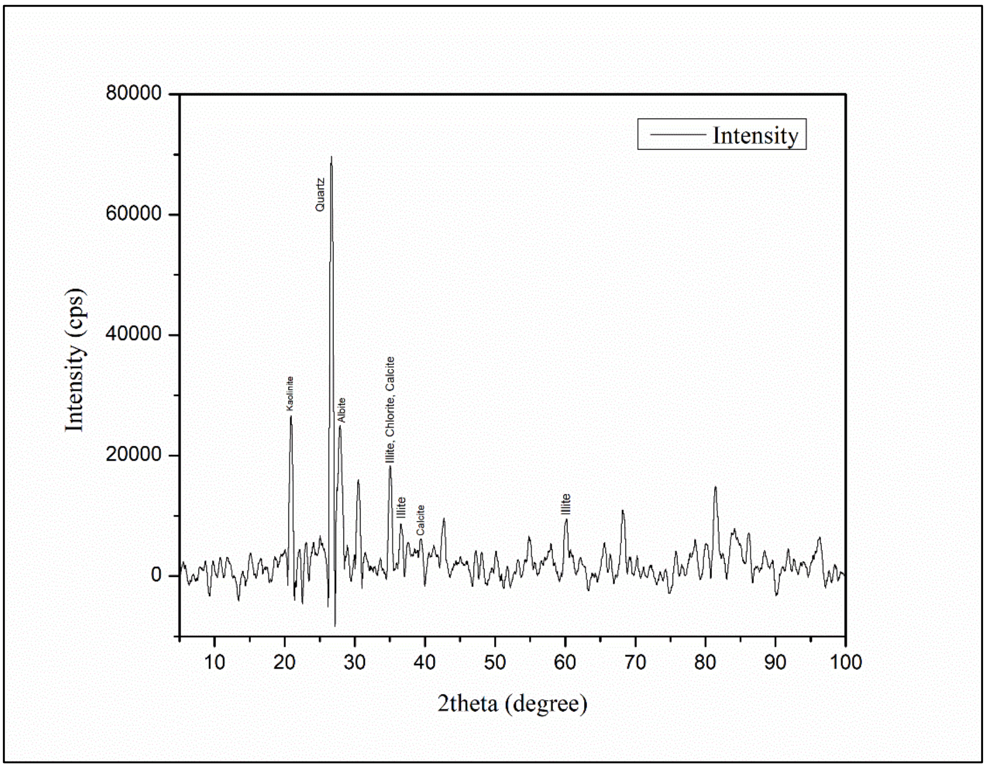
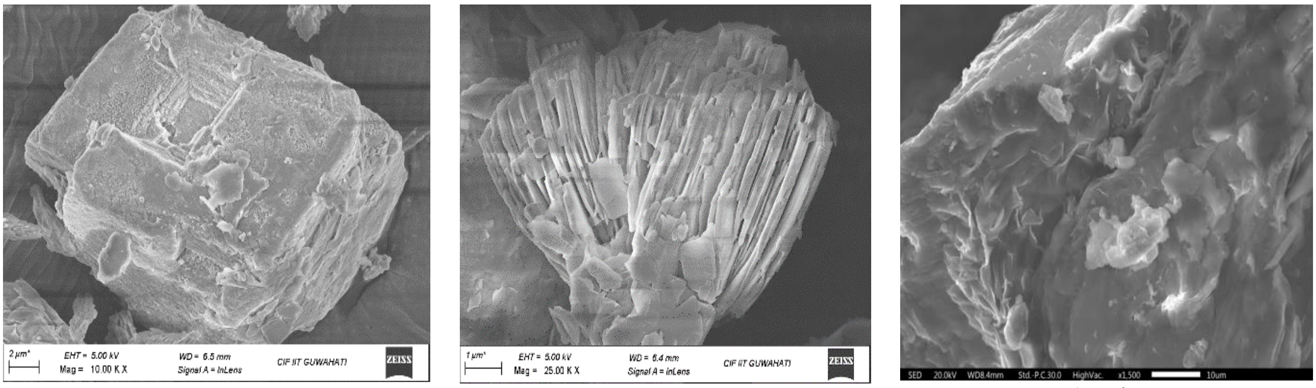


Figure 2: XRD image showing peaks of the identified minerals in the reservoir rock



a) Quartz b) Kaolinite c) Illite

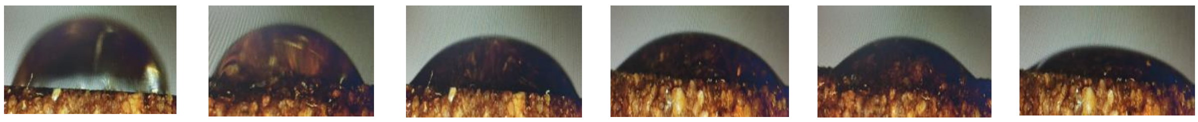
Figure 3: SEM - Photomicrograph of Kaolinite, Quartz and Illite

Figure 4 shows the CA of FW, DFW-3, DFW-5, DFW-7, DFW-9 and LSW and found CA decreases with dilution making the surface more water wet, which is in line with the results found by Teresa et al[28], Zhu et al[34], Kakati et al[12] and Shahib-Asl et al[24]. The following discussion demonstrates the change in wettability due to dilution of formation water and the mechanism is shown in figure 5.

Ions in high-salinity formation water are closely packed close to the rock surface, keeping the water oil-wet. Dilution decreases ionic strength which in turn expands the double layer around the clay particle[15,22,23,33]. Water may more easily replace oil because of this expansion, which lessens the attraction forces between the rock surface and oil components. Oil recovery improves when the rock surface gets more water wet. Formation water frequently contains divalent cations (Ca^{2+}, Mg^{2+}), which promote oil-wet conditions by bridging oil components (resins, asphaltenes) to the rock surface[4,25]. The concentrations of Ca^{2+} and Mg^{2+} are decreased by dilution which makes it harder for polar oil molecules to stick to the rock surface. Oil separates as a result and the rock surface gets wetter[12].

Zeta Potential (ZP): LSW and DFW injections are significantly influenced by the ZP and EDL thickness. Wettability change, oil detachment and EOR performance are all governed by these characteristics. Figure 7 showed Zeta sizer instrument where ZP experiment were performed and table 4 showed the results of ZP with dilution of FW with DW and comparison with LSW and EDL expansion and WA relation with ZP. Ionic strength reduces with dilution of FW, resulting in a higher negative ZP caused due to stronger electrostatic repulsion between the rock/brine and oil/brine interfaces[8,21,26]. A schematic representation showing the relation of Zeta potential magnitude to double layer around clay particle is depicted in figure 7[26]. The dependence of double layer thickness on ionic concentration around the mineral surface is portrayed in the figure. High salinity brine containing divalent cations keeps the double layer compressed, whereas low salinity water expands the double layer by replacing divalent cations with monovalent cations, promoting water wetness and improved recovery[13,16].

EDL expansion promotes water-wet conditions by decreasing attractive forces. The greater repulsion results from LSW produce a stronger negative charge (-42.5mV) which is like the results obtained by Mahani et al[18], Yang et al[33], Wei et al[31] and Elakneswaran et al[9]. ZP is improved by DFW; however, the whole wettability shift is limited since certain divalent ions (Ca2+ and Mg2+) are retained. EDL thickness expansion order is: DFW(Increasing) /LSF (Moderate) < LSW (Fully Expanded) < HSFW (Highly Compressed).



FW DFW-3 DFW-5 DFW-7 DFW-9 LSW

Figure 4: Decrease in contact angle with increase in dilution of formation water (shifting towards more water wet)

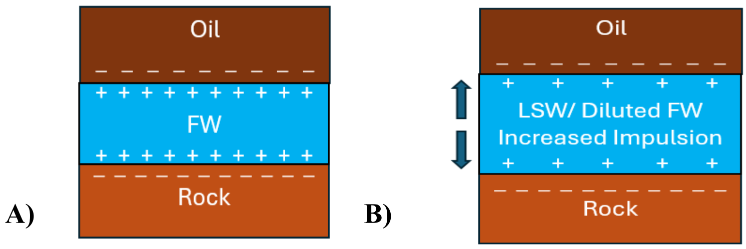


Figure 5: EDL expansion mechanism (A) Counter-ions adsorb to the FW/oil and FW/rock interfaces, (B) LSW/Diluted FW more repulsion between the two interfaces appears EDL as a thicker film

Table 4
Zeta Potential becomes more negative with dilution

Sample	FW	DFW-3	DFW-5	DFW-7	DFW-9	LSW
ZP	-23 mV	-26.5 mV	-29.2 mV	-33.5 mV	-38.6 mV	-42.5 mV
WA	Mixed-wet	Partial wettability shift to water-wet			Strong water-wet condition	
EDL	Compressed	Moderate expansion			Fully expanded	

Table 5
Change in parameters before/after flooding

Parameters	Conductivity (mS)		pH		ZP (mV)	
Flooding	Before	After	Before	After	Before	After
LSW	5.2	3.57	6.8	8.1	-42.51	-47.56
DFW-7	4.19	3.39	6.73	7.9	-33.53	-36.67

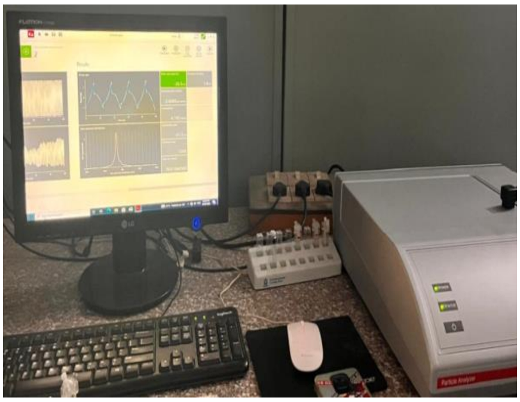


Figure 6: Zeta Sizer Analysis

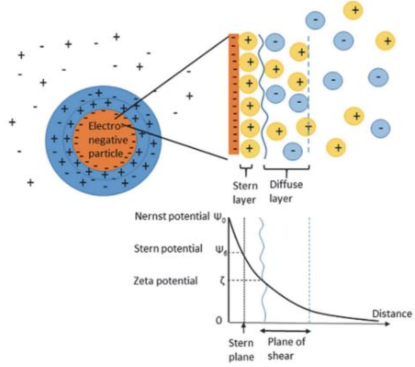


Figure 7: Schematic representation of electrical double layer[26].

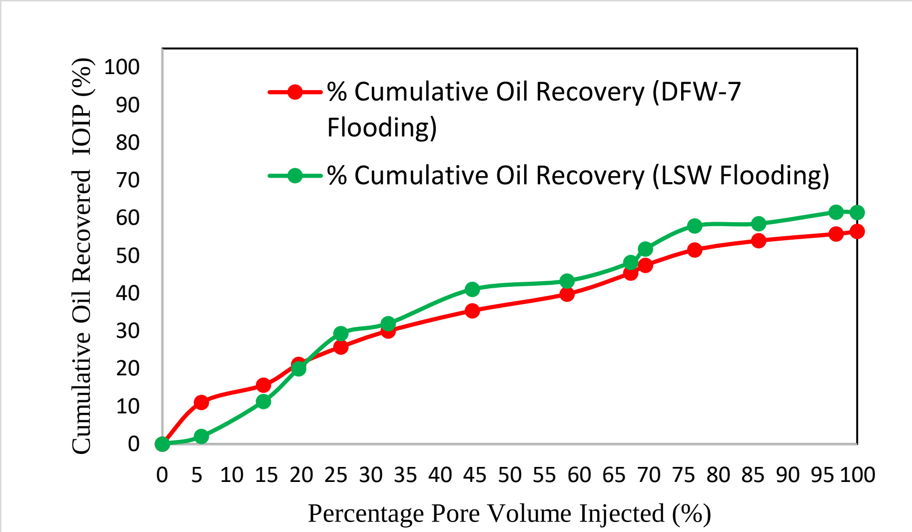


Figure 8: Coreflooding experiments

Coreflooding experiment: The core plug is placed in the Hassler core holder of the core flood apparatus at reservoir temperature 75ºC, the effective porosity is determined by the saturation technique and was found 25.17%. The following are the standard procedures for flooding operations: After the temperature equilibrium of 80ºC was attained, the first 3000 ppm brine flooding was continued to flood until the CP was saturated with brine. Secondly, the CP is flooded with CO until irreducible water remains. Brine flushes out the first initial oil saturation (Soi) during CO flooding. After CO flooding, again same concentration 300 ppm of brine flood is used to recover the Soi from the CP.

After the brine had completely permeated the Soi, the oil that had been washed away was subtracted to get the residual oil saturation (Sor). The prepared slugs were placed into the CP one at a time to recover that Sor. LSW achieved slightly better recovery than DFW-7 found recovery efficiency 61.44% and 56.41% IOIP respectively as shown in figure 8.

Change in conductivity, pH and ZP before/after flooding: The conductivity drops (DFW-7: 4.19 mS to 3.39 mS, LSW: 5.2 mS to 3.57 mS) indicated a decrease in ionic strength which causes the EDL expansion around the clay particles. Especially in sensitive clays like smectite, this expansion promotes swelling by increasing the electrostatic repulsion between clay minerals[5,17]. The clay used in the study is primarily dominated by kaolinite and illite. These clays are less swelling in nature compared to Smectite. The pH rise (DFW-7: 6.73 to 7.9, LSW: 6.8 to 8.1) raises the possibility of hydroxyl ion (OH^-) formation and CO used here is acidic in nature. Carboxyl (-COOH) can change the clay minerals surface charge. Although a higher pH often results in a stronger negative surface charge, which increases repulsion and may cause swelling. As already reported by Mahani et al[18] and Buckley et al[7], it can also cause the precipitation of divalent ions, such as Ca^{2+} and Mg^{2+} in case of DFW-7, which in certain situations can reverse swelling. Clay particle stability is revealed by the ZP measurements taken both before and after flooding (DFW-7: -33.5 to -36.67 mV, LSW: -42.5 mV to -47.56 mV). More negative ZP indicates more repulsion between clay particles, which raises the possibility of swelling. On the other hand, decreased electrostatic stability is indicated by a trend toward lower absolute ZP values (nearer to zero), which might result in particle flocculation and decreased permeability[5]. LSW showed more negative ZP change due to reduced ionic strength compared to DFW-7 and hence increasing electrostatic repulsion between clay particles. Ion exchange produces a more diffuse EDL and a higher potential for swelling by substituting monovalent Na^+ for divalent cations (Ca^{2+}, Mg^{2+})[3,17].

Conclusion

The following conclusions can be drawn on the basis of above investigations:

- LSW causes a more aggressive WA but also leads to higher risks of formation damage due to excessive swelling and permeability reduction. By tuning the ion composition and dilution, DFW-7 provides a balanced approach that enhances oil recovery without compromising rock integrity.
- DFW-7 shifted ZP to a more negative value (from –33.53 mV to -36.67 mV), improving electrostatic repulsion, controlling WA and LSW resulted in a stronger ZP shift (-42.51 mV to -47.56mV), which enhanced oil detachment but also led to excessive clay swelling and fines migration, risking permeability damage.
- The conductivity drops in case of DFW-7 flooding from 4.19 mS to 3.39 mS and in case of LSW flooding from 5.2 mS to 3.57 mS indicates a decrease in ionic strength which causes the EDL expansion around the clay particles. This expansion promotes swelling by increasing the electrostatic repulsion between clay minerals. XRD and SEM reveal the presence of Quartz, Kaolinite and Illite clays. These clays cause less swelling in nature compared to Smectite. The pH increases from 6.73 to 7.9 and 6.8 to 8.1 after DFW-7 and LSW flooding respectively. Although a higher pH often results in a stronger negative surface charge, which increases repulsion and may cause swelling, it can also cause the precipitation of divalent ions such as Ca^{2+} and Mg^{2+} which in certain situations can reverse swelling
- LSW achieved better recovery efficiency 61.44% IOIP than DFW-7 of 56.41% IOIP. Although LSW flooding can enhance oil recovery significantly, its uncontrolled clay swelling and fines migration pose risks for long-term formation stability and permeability. DFW-7 maintains a stable reservoir environment, ensuring optimal WA, clay stability and permeability retention, making it more suitable for field-scale applications.
- Future research should explore long-term reservoir performance, scaling effects and field implementation strategies to maximize EOR potential.

Hence, Ion-tuned DFW is an optimized, sustainable alternative to LSW, providing a balanced approach to EOR by enhancing oil recovery while minimizing formation damage.

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