

## Research Article

# Low Saline Water-Alkaline-Surfactant/Alternated/CO<sub>2</sub> Flooding in Reservoir Cores

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## Abstract

The discovery of new oil reserves has steadily declining over the years, so increasing the recovery factors from the oil fields is the only logical way to meet the growing demands. With this objective the different enhanced oil recovery (EOR) methods are designed. It has been observed that oil recovery by water flooding is influenced by the salinity and composition of injected water. Although low saline waterflooding (LSW) has the potential to recover additional oil, its recovery is less compared to chemical and gas EOR methods. The purpose of this study is to investigate the EOR potential of the novel low saline wateralkaline-surfactant/alternated/CO<sub>2</sub> (LSWASG) method in an oilfield of Assam, India. Reservoir cores, crude oils and formation water from an Upper Assam depleted oilfield were analysed for their characterization and for preparing the synthetic formation brine (SFB). Chemical formulations that will best recover crude oil were next screened based on interfacial tension (IFT) measurements. Finally, lab-scale core flooding experiments were conducted to evaluate the oil recovery potential of the proposed method. From the coreflooding experiments, it was observed that secondary water flooding of crude oil saturated core plugs resulted in recovery of about 33% oil originally in place (OOIP). Additional oil recovery by low saline waterflooding in the tertiary mode was 4.8 % OOIP.

However, the oil recovery with LSW combined with the selected formulation (0.5 wt% SDS + 1 wt% Na<sub>2</sub>CO<sub>3</sub>) with and without alternated CO<sub>2</sub> gas injection increased to 19.34% and 22.57% OOIP respectively. Higher oil recovery by the synergic combination of LSW, chemicals and CO<sub>2</sub> gas, highlighted the EOR potential of the novel LSWASG process in the Assam oilfield producing medium gravity crudes.

**Keywords:** Enhanced Oil Recovery, Low Saline Water Flooding, Alkaline-Surfactant Flooding, IFT Reduction, Coreflooding

## Introduction

Various studies done on EOR process, it has been proved that surfactant injection improves oil recovery by lowering the oil-water interfacial tension (IFT), also preventing capillary trapping of oil and/or remobilizing the trapped oil. During this process the efficiency could be reduced due to surfactant loss by adsorption and reduction of interfacial tension between water and oil. The surfactant retention increases with increasing salinity of the aqueous phase [1,2]. The multivalent ions are present in the water are dependent on the salinity of the formation water. The presence of divalent cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) in high-salinity water may cause precipitation and retardation of surfactant in porous media. Combination of surfactant with low-saline water containing low concentration of divalent ions may improve the performance of surfactant flooding in application with the enhanced oil recovery [3,4].

Hence low saline water flooding can be defined as the controlled salinity and composition of the injected water to become an emerging enhanced oil recovery technique. Modification of the water composition has shown to be an excellent way to increase recovery from both sandstone and carbonates. The research efforts of Webb et al. [5], Lager et al. (2006), and Lager et al. (2007) examined the low-salinity effect by conducting coreflooding experiments under reservoir condition. The laboratory results were validated by field trials including loginject-log, single-well chemical tracer, and interwell tests [4,6,7].

Decreasing the ionic strength by lowering the salinity in the brine would increase the electrostatic repulsion between the clay particle and the oil. The repulsive forces when the binding forces exceed, the oil is desorbed from the clay surfaces. Thus wettability alteration

will take place which will lead to a change in wetting phase toward increased water wetness. Reducing electrolyte concentration more, the electrostatic forces within the clay minerals will start to exceed binding forces, which might cause formation damage in real reservoir.

In this paper, the focus is placed on recent advanced application by combining the methods which can boost recovery and make it easier to in field application. In laboratory combining destabilization of oil layers during a Low saline Water Flooding with a low IFT environment is created that will prevents re-trapping of these oil layers.

The experiments are conducted in the cores of upper Assam basin. Combination with alkali surfactant mixture with low saline water can be more beneficial than low-salinity brine injection or surfactant flooding alone, since it increases oil recovery by additional lowering the IFT, and therefore can be more attractive economically.

The main motivation behind combining low salinity water and surfactant was to alleviate the operational challenges associated with surfactant flooding such as surfactant adsorption and oil trapping in porous media. We performed the low salinity water injection with alkali surfactant to the core and compare its performance to low-salinity water flooding alone and low-salinity flooding with alkali

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surfactant. We apply the mixture immediately after High saline injection without pre flushing the core with LSW to establish low salinity.

Therefore, the core flooding tests consist of low salinity-only core flooding, and combined low salinity and alkali. The experiments are designed such that first responsiveness of the system (oil-brine-rock) to low salinity is established. Then, on that basis, surfactant and alkali are combined and the recovery factors are compared.

## Experimental Analysis

### Materials used

Anionic surfactants together with a natural surfactant were. Anionic surfactant Sodium dodecylsulphate (SDS) used in the experiments was procured from Merck (India). Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), the conventional alkali, was purchased from Merck Specialities Pvt. Ltd., Mumbai. Sodium Hydroxide (NaOH), which adjusts the brine salinity, was purchased from Merck Specialities Pvt. Ltd., Mumbai. Formation water and porous media which were the reservoir rock samples (the core samples) were brought with courtesy from the upper Assam oil basin from two main producing reservoirs/sands of the oilfield from depths of (2500-2700) & (2900-3100) meters. The crude oil samples were obtained from the same producing horizons.

### Reservoir Rock, Crude Oil and Formation Water Analysis

Using Boyle's Law Double -Cell Method by measuring the bulk volume of the core plugs (using calipers) & grain volume the porosities of the reservoir rock samples were determined. The instrument used for porosity determination was the TPI-219 Helium Porosimeter, Coretest Systems, Inc, USA. Using Liquid Perm the liquid permeabilities of the core plugs were measured (Using Vinci Technologies, France) using the brine (3800 ppm NaCl) as the pore fluid. Three readings were taken for each core plug and their average was calculated.

For characterizing a particular reservoir fluid sample and also to make a preliminary assessment of the effectiveness of some EOR schemes, the laboratory analysis of crude oil should be done. For that, the crude oil sample was first separated from water using separating funnel at a temperature of 35°C. Procedure for crude oil analysis are as follows: (i) For the determination of density of crude oil samples, the ASTM D1298-67 [IP 150/68] hydrometer method was applied. (ii) Using the GRACE M3600 Viscometer, the dead oil viscosity of the oil samples was determined at the reservoir temperature. (iii) For determination of the pour points of the crude oil samples, the IP 15/67 method was followed. Pour point is measured to determine the temperature at which it will lose its flow characteristics. (iv) The asphaltene content of oil samples were determined by asphaltene precipitation with n-heptane (ASTMD2007-80). (v) According to Hubberd and Stanfield (1948), resin content was estimated. (vi) The acid number of the crude oils was determined by titration method.

Using Water Analyser (Make: Systronics; Model: 371), the pH and total dissolved solids (TDS) of the formation water sample were measured. The density was measured with ASTM hydrometer method and viscosity using Grace Viscometer. With the help of Flame Photometer (Make: Systronics; Model: 128), the positive ionic compositions like Na<sup>+</sup>, Ca<sup>++</sup> and K<sup>+</sup> were measured & Mg<sup>++</sup> was measured by titration with Ethylenediaminetetra acetic acid (EDTA). For the negative ionic compositions like Cl<sup>-</sup> and HCO<sub>3</sub><sup>3-</sup>, titration with AgNO<sub>3</sub> solution and alkalinity tests respectively were conducted. The physical and chemical properties of the formation water sample are listed in Table 2.

### Interfacial Tension Measurements

The formulations were further evaluated for IFT test to check

their ability in improving oil recovery with potential in reducing the oil-water IFT. Using a Grace M6500 Spinning Drop Tensiometer is used for determination of interfacial tension (IFT) between crude oil and surfactants solutions (6500 rpm, 850C rotation) was determined. The IFT was calculated using the Vonegut's equation under condition of drop length to diameter (L/D) greater than 4.

$$\lambda = \frac{\Delta\rho\omega^2}{4} r^3 \text{-----} 1$$

where  $\Delta\rho$  is the density difference between the crude oil and the surfactant solution, g/cm<sup>3</sup>;  $\omega$  is the angular velocity, rad/sec;  $\lambda$  is the IFT, mN/m;  $r$  is the radius of the drop in circular cylinder, cm.

### Core Flooding

The oil recovery factor from a flood by injecting a fluid into a core plug containing reservoir fluid is determined by laboratory core flooding analysis. The test is done at reservoir pressure and temperature. Figure 1 shows the schematic of the core flooding system. Gas and liquid enter a T-section right before the core inlet line. Pressure was measured at the inlet, mid sections of the core holder, and at the outlet. The core flood system consisted of two liquid pumps, CO<sub>2</sub> cylinder with regulator & mass flow controller (MFC), back-pressure regulator (BPR), coreholder, pressure transducers, data acquisition system, and heat chamber. The following procedure was adopted: (i) Pore Volume (PV) Determination: The PV of the dry & clean core plug was determined from its dimensions and its porosity. (ii) Brine Flooding: The prepared brine (3400 ppm) was used to saturate the core plug at room temperature (about 26 °C) and was driven by the pump. A number of PVs were run through the core at a constant flow rate to determine the permeability of the core to brine. (iii) Crude Oil Flooding: After brine saturation, the core flooding was done with crude oil. Oil saturation continues till the effluent is 100% oil cut. At the end of oil saturation, residual water saturation (S<sub>wi</sub>) and oil relative permeability at S<sub>wr</sub> are calculated. The oil-saturated core plugs were maintained at 70 °C for 30 hours to allow for possible wettability alteration. (iv) Low saline water Flooding: The prepared low saline water (1700 ppm) flooding was then carried out made from the original synthetic brine (3800 ppm). Residual oil saturation (S<sub>or</sub>) and water effective permeability at Sor (i.e. K<sub>w</sub>) are calculated at the end of waterflood.

## Results and Discussion

### Reservoir Rock, Crude Oil & Formation Water Analysis

Core analysis was done with 1.5 inch diameter cleaned & dried sandstone core plugs. The porosities & absolute permeabilities of the core plugs from depth of (2900-3100) meters were in range of 17.62 – 18.62 % and 2 - 3 md respectively. For shallower depth (2500-2700 meters) core plugs, the respective values were in the range of 24.64 – 25.15 % and 25– 30 md. An inverse correlation was observed between

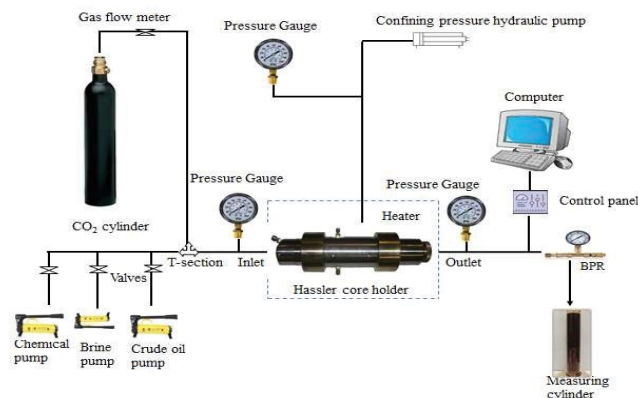


Figure 1: Schematic diagram of Laboratory Core Flooding System.

these rock properties and depth for oilfield. The most obvious reason for this inverse relation is owing to the combined effects of compaction and cementation [8].

Table 1 presents the results of the crude oil analyses performed. Crude oils are classified according to the API gravity as: (a) Light crude oil has API gravity higher than 31.1°; (b) Medium oil has API gravity between 22.3 and 31.1°; (c) Heavy crude oil has API gravity below 22.3°. The API gravities of the crudes were found to be in the range from 22.81° to 30.96° API. So the crude oils of the oilfield are medium gravity.

The dead-oil viscosity of crude oil is the viscosity at atmospheric pressure (no gas in solution) and system temperature. The dead oil viscosities of the crudes under study were measured at reservoir temperature of 165°F (74°C). Viscosity of crude oils plays an important role during its recovery. High viscosity leads to high remaining oil saturation after waterflooding operation and conformance problems during chemical & gas EOR processes.

The pour points of almost crude oils were high 24° to 27°C. High-pour-point crude oils generally have pour points in the range from 15 to 52°C and may be solid at room temperature (27°C). This higher value of pour point is generally associated with crude oils of high paraffin content and lower value of pour point with crudes of more aromatic nature.

Assam crude oils are reported to have higher pour points 30°C and higher wax content (11wt %) [9,10]. The high pour points of the crudes oil samples under study may be attributed to their waxy nature.

Asphaltenes are the polar, polyaromatic, high molecular weight hydrocarbon and wax-free fraction of crude oil that are soluble in toluene, but insoluble in alkanes (n-heptane to npentane) [11]. Asphaltenes tend to remain in solution under reservoir temperature and pressure conditions stabilized by resins adsorbed on their surface. Asphaltenes may start to precipitate if the stability with crude oil is destabilized caused by changes in temperature and/or pressure during primary depletion. Asphaltenes may also become unstable as a result of co-mingling of fluid streams as well as by gas injection during improved oil recovery (IOR) operations [12]. In CO<sub>2</sub> flooding, the asphaltene-to-resin ratio of crude oil is altered causing asphaltene precipitation and thereby its deposition [13]. This is one of the major problems that confront petroleum engineers during a CO<sub>2</sub> flooding project. Resins have the effect of keeping asphaltenes in solution. A high resin to asphaltene ratio (R/A) indicates that asphaltenes are less likely to come out of solution [14]. Leontaritis et. al. (1987) presented a condition for asphaltene stability as follows: R/A > 3.0 as Steady state, 2.0 < R/A < 3.0 as Meta-steady state & R/A < 2.0 as Unsteady state [15,16]. The R/A for the crudes all the reservoirs are greater than 3, so based on the Leontaritis criterion, there is enough amounts of resins for asphaltene stabilization in all the reservoirs.

Acid number is measure of the amount of acidic components present in a crude oil. It is expressed as the milligrams of KOH that is required to neutralize 1 gm of oil sample. In alkaline flooding, in situ

Table 1: Crude oil analysis.

Properties	Sample 1	Sample 2
Name of reservoir	TS-5	TS-2
Average Depth (meters)	2400-2800	2700-3200
Density (Kg/m <sup>3</sup> ) at 60 °F	920	883
API gravity	23.54	31.33
Dead oil Viscosity (cP)	9.6	4.7
Pour point (°c)	29	23
Asphaltene content (%)	0.62	1.61
Resin content (%)	5.51	16.87
Acid number	1.5	2.3

soap is generated by reaction of alkali agents such as sodium carbonate with acids in crude oil. For a reservoir to be a good candidate for alkaline flooding the acid number of the crude oil should be at least 0.5 ml/g. Crude oils with acid number > 0.5mg KOH/g are known as acidic crudes. The acid numbers of all the crude oils are above 0.5mg KOH/g indicating acidic nature of the crudes [17-19].

Based on the above crude oil analysis, it found that the crude oils of the reservoirs are medium gravity and having high pour points can be inferred as waxy. The asphaltene of the crudes was found to be in the stable state as the resin content was high enough for its stability. Based on this preliminary assessment of the crudes, the oilfield was found to be most suitable for the application of CO<sub>2</sub> flooding and ASG process.

Table 2 lists the physical and chemical properties of the formation water sample. Based on the compositional analysis of reservoir formation water, synthetic formation brine (SFB) was prepared. Low saline reservoir brine was prepared by diluting the SFB with distilled water in 0.5 volume ratio.

### IFT Measurements

Figure 2 (a) and (b) shows the oil-water IFT behaviour of SDS at various concentration and 0.5 wt% SDS with Na<sub>2</sub>CO<sub>3</sub> alkali at various concentration respectively. The IFT decreased with increasing surfactant/alkali concentration upto a certain concentration and then was almost constant. The concentration with the lowest value of IFT was taken as the optimum concentration. The optimum concentration obtained at: SDS = 0.5 wt% and Na<sub>2</sub>CO<sub>3</sub> = 1 wt%. The lowest IFT achieved with surfactant-alkali combined was 2.1 x 10<sup>-2</sup> mN/m. The IFT decreased with increase in SDS concentration upto 0.5 wt%, and then was almost constant with further increase in concentration. The reason for this behavior could be attributed to the increase in the amount of surfactant molecules adsorbed on the oil-water interface with the increase in the surfactant concentration which reduced the oil-water IFT. But after a certain concentration, the surfactant molecules adsorbed on the oil-water interface was saturated with no further adsorption and so a constant IFT value was obtained.

Table 2: Physical and chemical properties of formation water

Property	Measured Value
Density, Kg/m <sup>3</sup> (at 30 °C)	1023
Viscosity, cP (at 30 °C)	0.95
pH (at 30 °C)	8.32
Total dissolved solids (mg/L)	3528
Sodium (Na <sup>+</sup> ) (mg/L)	1570
Calcium (Ca <sup>++</sup> ) (mg/L)	88
Potassium (K <sup>+</sup> ) (mg/L)	13
Magnesium (Mg <sup>++</sup> ) (mg/L)	19

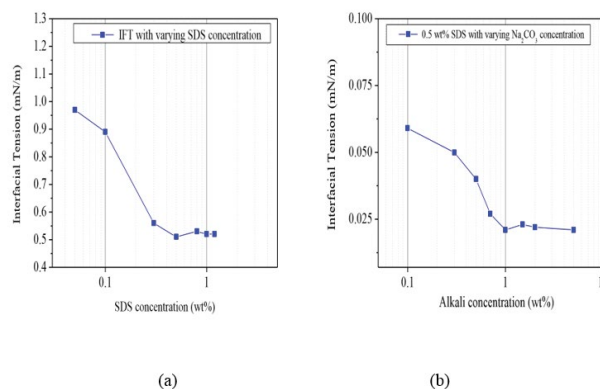


Figure 2: Oil-water IFT of (a) SDS and (b) SDS + Na<sub>2</sub>CO<sub>3</sub>



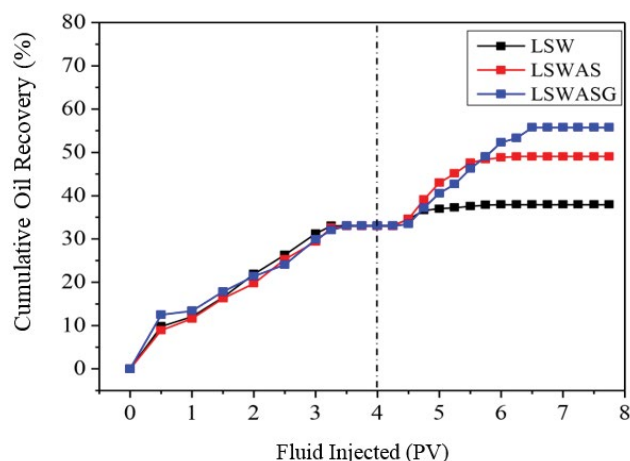
To obtain the alkali-surfactant (AS) formulation that can achieve ultralow IFT with the crude oil, different concentration of Na<sub>2</sub>CO<sub>3</sub> were evaluated to investigate their capability to reduce oil-water IFT to ultra-low value (equalling 10<sup>-2</sup> or 10<sup>-3</sup> mN/m). The IFT was observed to decrease with the increase of alkali concentration upto a certain point. The reason for this decrease in the IFT value was due to in-situ surfactants generation caused by the reaction between alkali and acidic components of crude oil. A highly oil-soluble single pseudo-acid component (HA) is assumed to be present in oil which partitions into the water phase upon coming into contact with water. Due to the hydrolysis of Na<sub>2</sub>CO<sub>3</sub>, OH<sup>-</sup> ions are produced which react with HA to produce natural soaps NaA (which acts as a surfactant). With the increase in alkali concentration, the concentration of A<sup>-</sup> increased which decreased the oilwater IFT. But, the IFT would not decrease further beyond a certain optimum concentration as the concentration HA was limited in the crude oil. For the reasons described in the foam stability section, the alkali Na<sub>2</sub>CO<sub>3</sub> was selected for the coreflooding experiments. Also, 1 wt% Na<sub>2</sub>CO<sub>3</sub> was selected as the optimum concentration with 0.3 wt% SDS because of the lowest IFT achieved at this concentration.

### Core flooding experiments

In this part, the results of coreflooding experiments are presented and described based on the oil recovery data. The tests were done at various pressures and reservoir temperature. The identified chemical formulations based on the IFT results were used in the core floods. In coreflood 1, the oil saturated core plug was subjected to water flooding with synthetic formation brine. The oil recovery by water flooding after injection of 4 PV of SFB was 33.2 % OOIP. In coreflood 2, the oil recovery after injection of 4PV SFB was 33 % OOIP. This was followed by low-salinity water which increased the oil recovery by 4.8% OOIP. Coreflood 3 was similarly conducted by injecting 4 PV of SFB into the core plug saturated with crude oil which resulted in oil recovery of 32.97 %OOIP. The injected was then switched over to low saline brine plus the optimum alkali-surfactant formulation. The resulting additional oil recovery substantially improved to 19.34% OOIP. Higher recovery during this process is attributed to the decrease in the oil-water IFT caused by the addition of alkali-surfactant to brine. The IFT results indicated that addition of alkali-surfactant can sufficiently lower the oil-water IFT value. With the decrease in the IFT, the capillary number became quite large to mobilize trapped oil leading to increase oil recovery. Coreflood 4 was conducted to investigate the effect of synergic combination of LSW, chemicals and CO<sub>2</sub> gas on recovery. SFB was first injected for about 4 PVs to recover 33% OOIP. The experiment was switched to low-salinity water with alkali-surfactant alternated with CO<sub>2</sub> gas injection. During the process, 1 PV of low-saline water with alkali-surfactant was alternated with 1 PV of CO<sub>2</sub> gas and followed by 2 PV of low saline chase water. The additional oil recovery improved to 22.74% OOIP highlighted the EOR potential of LSWASG. Figure 3 shows cumulative oil recovery versus the injected fluid pore volume by the above processes. As most of the residual oil is produced during the first two cycles of LSW with chemicals and gas injection, little oil is produced during the chase waterflooding. The additional oil recovery during the LSWASG flooding could be attributed to a number of factors including the wettability change, IFT reduction, CO<sub>2</sub> injection causing oil swelling and oil viscosity reduction; foam formation due to alternate chemical/gas injection etc.

### Conclusions

From the analysis of crude oil, it was observed that crudes are medium gravity with high waxy content. The crudes were acidic indicating the applicability of alkali injection for EOR. The asphaltene of the crudes was found to be in the stable state with high resin content, so CO<sub>2</sub> injection is possible without the asphaltene precipitation



**Figure 3:** Cumulative oil recovery versus the injected fluid pore volume.

problem. The rock porosity of the oilfield was found to bear an inverse correlation with the depth. An optimum concentration of surfactant and alkali existed at which lowest value of oil-water IFT was obtained. Ultra-low IFT ( $2.1 \times 10^{-2}$  mN/m) was obtained with the optimum formulation (0.5 wt% SDS + 1 wt% Na<sub>2</sub>CO<sub>3</sub>) demonstrating its EOR potential. The highest oil recovery of 22.74% OOIP obtained by the combination of low-saline water, alkali-surfactant and CO<sub>2</sub> gas illustrated the synergism of the hybrid EOR process. A number of factors including the wettability change, IFT reduction, CO<sub>2</sub> injection causing oil swelling and oil viscosity reduction; foam formation due to alternate chemical/gas injection were expected to play their role in recovering incremental oil during the LSWAG process.

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