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ORIGINAL PAPER - PRODUCTION ENGINEERING

Impact of new foam surfactant blend with water alternating gas injection on residual oil recovery

Muhammad Khan Memon[1] · Khaled Abdalla Elraies[1] · Mohammed Idrees Al-Mossawy[1]

Abstract Enhanced oil recovery methods are the future of maximizing oil recoveries. Any incremental oil recovery can support the world economy by producing more oil at a minimum price. The surfactants are the major constituent of the injection fluids for EOR applications. Addition of foam-generated surfactants in water alternating gas injection is one of the potential solutions for reducing the gas mobility and improving sweep efficiency, but the major challenge of surfactants used with water alternating gas injection is its stability in presence of formation water and crude oil at reservoir conditions. The objective of this study is to investigate the stable surfactant as a foaming agent to improve the efficiency of residual oil and reduce the gas mobility. To achieve this main objective, individual and new surfactant blended formulations were evaluated with injection water and crude oil in the porous media at 96 °C and 1400 psi. Experimental result showed that generated foam in presence of crude oil has reduced gas mobility which provides good indication of CO_2 mobility control and improves sweep efficiency. Oil recovery based on original oil-in-place by surfactant blend of 0.6 wt% AOS + 0.6 wt% TX 100, 0.6 wt% AOS + 0.6 wt% LMDO and individual surfactant of 0.6 wt% AOS were recorded as 91.9, 83.7 and 72.66%, respectively. Foam stability in presence of crude oil, reduction in gas mobility and increase in oil recovery indicated that these surfactant blends are good foaming agents as compared to individual surfactant in enhanced oil recovery applications.

Introduction

The first reported water alternating gas (WAG) field pilot was implemented in the North Pembina field, Alberta, Canada in 1956–1957 (Algharaib et al. 2007; Nadeson 2004). At present, the WAG injection process has been applied in oil fields of USA, Canada, Malaysia, Norway and some other countries of the World. In this process, mainly CO_2 or combination of CO_2 and produced hydrocarbon gases are injected at miscible or immiscible conditions. However, WAG injection process suffers by gravity segregation and viscous fingering mostly in heterogeneous reservoirs (Rogers and Grigg 2000). Therefore, the incremental oil recovery during WAG injection remains low. Controlling the mentioned problems in water alternating gas injection, addition of foam (surfactants) in brine water is more efficient. Foam-generating surfactants flooding has been paid more attention in enhanced oil recovery (EOR) methods due to its unique properties of oil displacement and gas mobility control (Svorstol et al. 1996; Wang et al. 2009). The method has attracted increasing attention of oil industries and research institutions. The performed theoretical and experimental studies, pilot tests and field application showed that the foam used as gas mobility control can improve the EOR process. The foam stability at reservoir conditions in the North Sea, Daqing oil and other fields proved the potential of this method (Feng et al. 2009; Vikingstad et al. 2006; Wang et al. 2006).

✉ Muhammad Khan Memon
  mkmemon@hotmail.com

[1] Petroleum Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Tronoh, Perak Darul Ridzuan, Malaysia

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Foam injection in oil reservoir was first proposed by Bond and Holbrook and reported by Bernard and Holm in 1965 (Boud and Holbrook 1958; Bernard and Jacobs 1965). Foam is defined as a dispersed system consisting of bubbles that are separated by foam film and plateau boarders (Karakashev and Grozdanova 2012). In porous media, foam surfactants are used in near wellbore flow treatments such as foam–acid matrix stimulation and plugging of unwanted phases (Chang et al. 2002; Wassmuth et al. 2004), in fractured fluids (Blauer and Kohlhaas 1974; Wheeler 2010), in shallow subsurface environmental remediation (Hirasaki et al. 1997; Mamun et al. 2002; Hirasaki 1989) and in EOR processes to control the gas mobility and overcome in situ permeability variations (Blaker et al. 2002). This method can be applied by simultaneously injecting gas and surfactant solution or alternating gas with brine-added surfactant solution (Dholkawala et al. 2007).

The world's largest foam application was implemented successfully on the Snorre field. The main purpose of foam was used with WAG injection process as gas mobility reduction. The field is located in Norwegian sector of the North Sea, about 200 km northwest of Bergen. A foam injection was started in July 1996. AOS_{C14-16} was used during foam cycle with 1–2 wt% concentration. 50% GOR was reduced for 2 months. Gas injectivity was reduced during the first and second gas cycle. This is because of foam generated and because the foam zone extended during first and second gas cycle (Sheng 2013). The important experience by this project is the good understanding of foam behavior at the target reservoir conditions that led to good planning and successful field application (Farzaneh and Sohrabi 2013).

In recent years, many foaming agents were selected and studied to achieve the best foam stability in presence of crude oil (Al-Attar 2011; Kovscek et al. 2010; Deng et al. 2012; Ashoori et al. 2011; Lai and Chen 2008; Cubillos et al. 2012). Most of the research has been carried out on individual (single) surfactant as a foaming agent, but has neglected the effect of blend of foam surfactant system. Surfactants are the major constituent of the injection fluids for EOR applications. In this research study, we used consolidated Berea sandstone core samples to perform core flooding experiments in order to examine the effectiveness of surfactant blended formulations at reservoir conditions. Blend of surfactant solutions synergistically exhibits better foaming properties and will open new opportunities to produce more residual oil from depleting oil reservoirs. This research focuses on the study of individual and blend of foam surfactants as a foaming agent that has better gas mobility reduction and thus improving overall efficiency of residual oil.

Experimental work

Materials

Foam surfactant

Three commercially available surfactants were used to perform the experiments. Alpha olefin sulfonate (AOS_{c14-16}) and lauramidopropyl amine oxide (LMDO) were supplied by Stepan Company, USA. Octylphenol ethoxylate surfactant (Triton TX-100) was purchased from Sigma-Aldrich. The molecular weight of each surfactant is known. All surfactant were used as received without further treatment.

Synthetic brine (injection water)

Sodium chloride (NaCl) was purchased from Fischer Company, UK, magnesium chloride ($MgCl_2 \cdot 6H_2O$), potassium chloride (KCL), sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2So_4) and calcium chloride ($CaCl_2 \cdot 2H_2O$) were purchased from R & M Chemicals, UK. The field-related brine with 34107 ppm was synthesized in the laboratory and used as injection water. Table 1 presents the composition of injection water.

Crude oil

Crude oil was collected from oil field offshore Malaysia. The density was measured as 0.7886 g/cc (49.2307Ib/ft^3) at 96 °C and 1400 psi by Anton Paar density meter. The oil viscosity was measured as 1.591cp at 96 °C and 1400 psi by HTHP EV-1000 viscometer. The specific gravity of crude oil is 0.7889, and degree API is 37.7.

CO_2 gas

CO_2 gas was selected due to its miscibility/partial miscibility with many hydrocarbon components of crude oil at

Table 1 Composition of injection water

Salt	mg/liter
Sodium (Na)	10,603
Chloride (Cl^{-1})	18,807
Calcium (Ca)	354
Magnesium (Mg)	1219
Potassium (K)	325
Bicarbonate (HCO_3^{-1})	163
Sulfate (So_4^{-2})	2636
Total salinity (ppm)	34,107

Table 2 Properties of CO_2 gas

Properties	Result
Apparent molecular weight	44
Density of CO_2 (Ib/ft^3)	11.58,155 (0.1854 g/cm^3)
Viscosity of CO_2 (cp)	0.0184 at 96 °C
Critical temperature (°C)	31.1
Critical pressure (Psi)	1070

Table 3 Properties of Berea sandstone core samples

Properties	Core A	Core B	Core C
Diameter of core sample (cm)	3.81	3.83	3.82
Length of core sample (cm)	7.66	7.60	7.69
Area of core sample (cm^2)	11.34	11.40	11.4
Pore volume (cm^3)	16.5	16.7	16.8
Bulk volume (cm^3)	86.87	86.87	86.8
Porosity (%)	19	19.2	19.3
Permeability to brine, (mD)	165	164	171

reservoir conditions. Gas viscosity at 96 °C was calculated by Sutherland's equation. This equation is based on kinetic theory of ideal gases (http://www.lmnoeng.com).

$$\mu = \mu_o \left(\frac{a}{b}\right)\left(\frac{T}{T_o}\right)^{3/2} \qquad (1)$$

$$a = 0.555T_o + C$$

$$b = 0.555T + C$$

For CO_2 gas, μ_o = reference viscosity at reference temperature, 0.01480cp, T_o = reference temperature, 527.6°R, and C = Sutherland constant, 240.

Density of CO_2 gas was calculated at 96 °C and 1400 psi by using the following formula. Properties of CO_2 gas are presented in the Table 2.

$$\rho_{CO_2} = \frac{PM_a}{ZRT} \qquad (2)$$

where ρ_{CO_2} = Density of gas, Ib/ft^3, M_a apparent molecular weight of gas, P = pressure, psi, R = gas constant, T = temperature, °R, Z = CO_2 gas compressibility at 96 °C and 1400 psi (Z = 0.746).

Berea sandstone

Berea sandstone is considered as an excellent sandstone for the laboratory experiments particularly in EOR processes. Berea sandstone is a sedimentary rock whose grains are predominantly sand-sized and are composed of quartz sand held together by silica. These core samples possess a chemical resistance to the erosive action of the acidic chemicals. Properties of these cores are presented in the Table 3.

Core flooding

The core flood apparatus from Sanchez Technologies, France, was used for foam/oil interaction in porous media experiments. The system consists of two automatic displacement injection pumps, back pressure regulator to maintain the pressure, a gas collector, a core holder which is assigned in an oven, three high-pressure accumulators

and syringe pump for injecting CO_2. Figure 1 presents a schematic diagram of core flooding experiment. Berea sandstone core was loaded in the core holder. The core holder was placed horizontally in all experiments. Distilled water was pumped in the annular space between the core holder to maintain the confining pressure. Three high-pressure accumulators were used to store and deliver crude oil, brine and surfactant blend solution. After that, these accumulators and core holder were placed in an oven at 96 °C and 1400 psi. Two automatic displacement pumps were used to displace crude oil, brine and surfactant blend solution through Berea sandstone core that was placed inside core holder. The back pressure regulator was used to maintain the pressure in the system. The back pressure during experiment was set 1400 psi which is equal to average pressure of operating reservoir. Recovered volumes of produced oil and water were measured by graduated cylinder.

Displacement steps

Water injection

To measure the absolute permeability of the Berea sandstone core sample, injection water was injected with injection rate of 0.2 cm^3/min. Darcy equation was used to calculate the permeability.

Crude oil injection

The crude oil was injected at 0.2 cm^3/min through the Berea sandstone core (brine saturated) until no more brine was produced. Irreducible water saturation (S_{wi}) can be determined through oil drainage process. This simulates the first migration of crude oil to the reservoir rock where crude oil is gradually replacing the original wetting phase. At this step, oil permeability at irreducible water saturation can be determined. Original oil drainage process (OOIP) can be calculated by Eq. (3).

$$OOIP = V_p(1 - S_{wi}) \qquad (3)$$

Fig. 1 Schematic diagram of core flooding
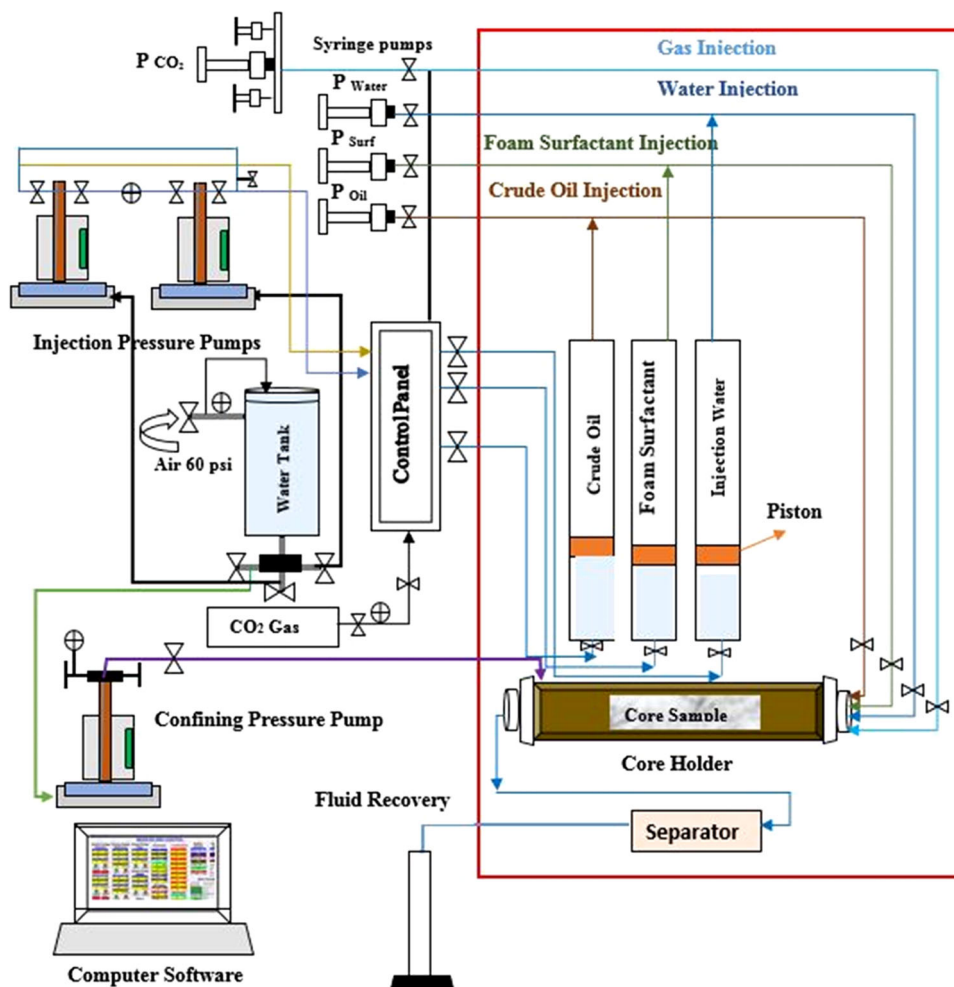
To establish the interaction between crude oil and Berea sandstone core, aging procedure was performed at same reservoir conditions.

Water flooding

Synthetic brine was injected at 0.2 cm^3/min through the Berea sandstone core until 100% water cut. At this step, the residual oil saturation to water injection was measured. The residual oil saturation (S$_{or}$) can be calculated from Eq. (4).

$$S_{or} = \frac{(OOIP - V_o)}{V_p} \tag{4}$$

Incremental oil recovery was calculated by using material balance equations including the oil left behind in the oil flooding and oil produce during different stages of flooding. The recovery factor (RF) at each step of oil production by injection of brine or gas can be calculated from Eq. (5).

$$RF = \frac{V_o}{OOIP} \times 100 \tag{5}$$

SAG flooding

Two equal cycles of surfactant alternating gas were injected with injection rate of 0.2 cm^3/min. The purpose is to check the performance of selected surfactant blend formulations for residual oil recovery after water flooding. Equal ratio 0.3PV of CO$_2$ and 0.3PV of surfactant was injected in each cycle. The recovered volume of crude oil and brine in the graduated cylinder was noted. The oil recovery and residual oil saturation were calculated by volume of residual oil produced using material balance equations.

Results and discussion

Before core flooding experiment, interfacial tension (IFT) between injection water and crude oil was tested by spinning drop tensiometer. Selected surfactant formulations for core flooding experiment were reduced IFT between injection water and crude oil. The IFT between injection

Table 4 IFT values of injection water, crude oil, surfactant AOS and AOS blend formulations

ID	Formulations	IFT (mN/m)
1	Brine/crude oil	9
2	0.6% AOS	0.94
3	0.6% AOS + 0.6% TX 100	0.88
4	0.6% AOS + 0.6% LMDO	1.24

Table 5 Fluid saturation properties

Properties	Core A	Core B	Core C
Drainage flow rate, (cm^3/min)	0.2	0.2	0.2
Imbibition flow rate, (cm^3/min)	0.2	0.2	0.2
Irreducible water saturation	0.35	0.36	0.32
Residual oil saturation (after water flood)	0.4	0.42	0.41
Test temperature, (°C)	96	96	96
Test pressure, (psia)	1400	1400	1400

water, crude oil and surfactant solutions is presented in the Table 4. Core flooding experiments were performed to investigate the impact of three foam surfactant formulations on gas mobility and residual oil recovery. Berea sandstone core A, B and C were used for displacement tests. Table 5 presents fluid saturation inside a core during core flooding. After primary imbibition and establishing of residual oil saturation, the injection process is followed by CO_2 flooding and surfactant alternating gas injection process. Table 6 presents the displacement steps performed on core flooding experiments. The pressure drop during the displacement is correlated with the recovery due to in situ generation and foam propagation.

Foam/crude oil interaction (core sample A)

After water flooding, CO_2 (gas flooding) was injected with injection rate of 0.2 cm^3/min. At the initial stage of gas injection, low volume of oil with water production was recovered. After continuous injection at the same flow rate, oil is produced at the exist point. The oil drop contains some gas bubbles, which can be attributed to the gas dissolution mechanism for residual oil recovery. At this point, gas breakthrough was not observed. The gas breakthrough can be detected by observing the bubbles of gas that appeared at the effluent recovery test tube. After gas breakthrough, the oil was recovered as the effluent like mixture of oil and gas. Figure 2 presents oil produced during gas flooding after gas breakthrough (mixture of oil and waxy components).

Surfactant blend of 0.6% AOS + 0.6% TX 100 solution followed by CO_2 was injected with constant rate of 0.2 cm^3/min. Two cycles of SAG1 and SAG2 with equal slug size of 0.3PV were injected. Differential pressures by SAG1 and SAG2 injected cycles were compared. Figure 3 presents the Δp profile of CO_2 flooding and CO_2 slug of SAG1 and SAG2 injection. CO_2 injected in the first cycle of SAG1 showed increase in Δp which is inferred stable foam inside the core. The increase in Δp of CO_2 slug is due to the injected slug of foam surfactant blend before injection of CO_2 slug. The differential pressure curve starts to decrease after its maximum value. This maximum Δp corresponds to the foam breakthrough at the outlet. The decrease in Δp after breakthrough is because of the bubble coalescence due to diffusion or breaking of foam films (Yu et al. 2014). However, the decrease in Δp after foam breakthrough for this core sample A was very small. It indicates that the foam generated by this sample was stable and little foam coalescence occurred during the displacement process. Foam was not generated by CO_2 slug in second cycle after second injected slug of surfactant solution due to high gas saturation. During gas displacement in the core, one possible reason is that, CO_2 is not completely dispersed in to the surfactant solution to form a foam bank as a result the value of Δp remains low. Table 7 presents the amount of oil

Table 6 Displacement steps for core sample A, B and C

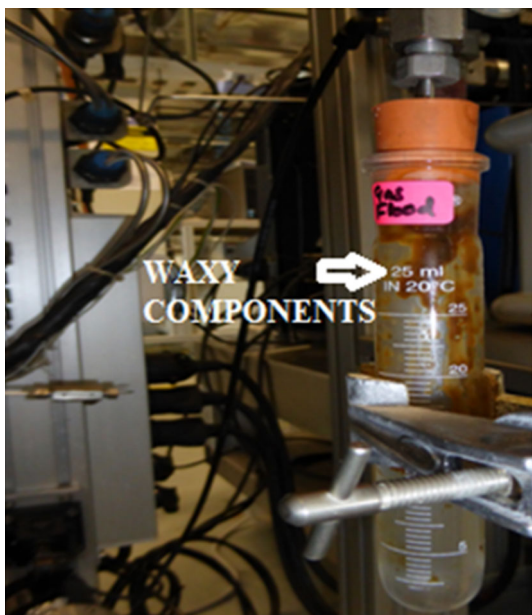| Displacement steps	Injected fluid	Flow rate (cm^3/min)	Slug size core A (PV)	Slug size core B (PV)	Core C	
					Flow rate (cm^3/min)	PV
Brine injection	Brine	0.2	2	2	0.8	2
Crude oil	Crude oil	0.2	2	2	0.8	2
Water flooding	Brine	0.2	2	2	0.24	2
Gas flooding	CO_2	0.2	0.3	0.3	0.24	0.3
SAG1	Surfactant	0.2	0.3	0.3	0.24	0.3
	CO_2	0.2	0.3	0.3	0.24	0.3
SAG2	Surfactant	0.2	0.3	0.3	0.24	0.3
	CO_2	0.2	0.3	0.3	0.24	0.3

Fig. 2 Oil produced during gas flooding after gas breakthrough (mixture of oil and waxy components)
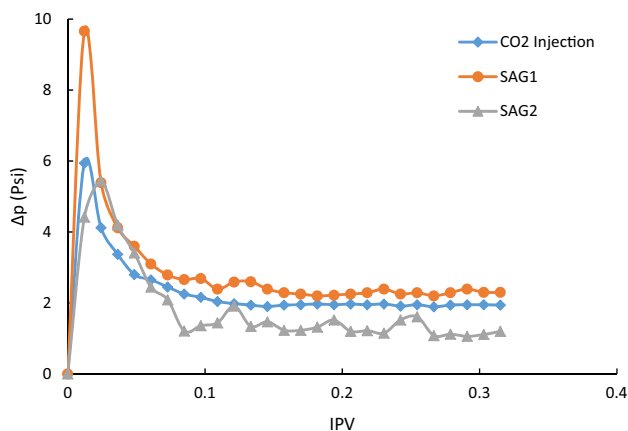

Fig. 3 Δp profile of CO_2 flooding, CO_2 slug of SAG1 and SAG2 injection (0.6% AOS + 0.6% TX 100)

Table 7 Oil recovery based on OOIP (0.6% AOS + 0.6% TX-100)

Injection steps	Oil collected (ml)	RF (%)
Water flooding	4.10	38.46
Gas flooding	1.5	52.46
Surfactant solution	1.7	68.4
Gas	2	87.16
Surfactant solution	0	87.16
Gas	0.5	91.9

recovered and recovery factor (RF) based on original oil-in-place (OOIP).

The increase in volume of recovered residual oil is due to the formation of macroemulsion inside the core after the
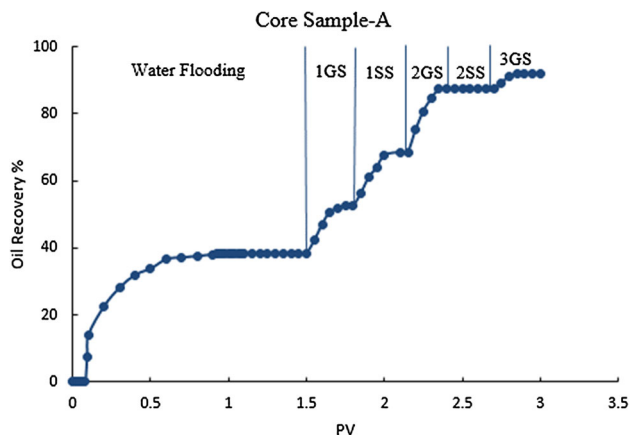
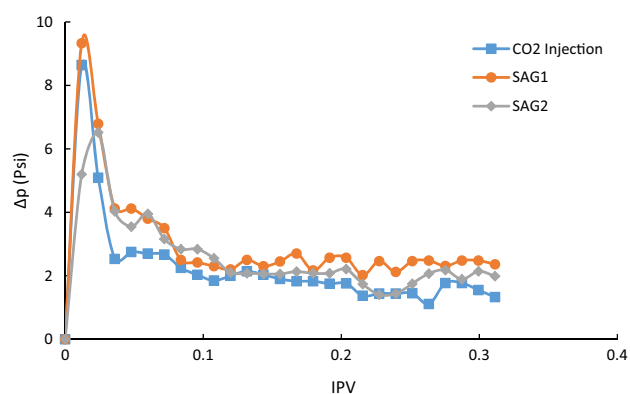**Fig. 4** Oil recovery by surfactant blend of 0.6% AOS + 0.6% TX-100

Fig. 5 Δp profile of CO_2 flooding, CO_2 slug of SAG1 and SAG2 injection 0.6% AOS + 0.6% LMDO

first slug of foam injected and foam breakage. Further, the microemulsion prevents the injected surfactant blend slug from generating the foam. Figure 4 presents the oil recovery by new surfactant blended formulation of 0.6% AOS + 0.6% TX-100. Maximum residual oil recovery resulted from new surfactant blend of 0.6% AOS + 0.6% TX-100 due to delay breakthrough time. Delay in breakthrough time increases the macroscopic efficiency and oil recovery consequently, as oil recovery in any displacement process depends on the volume of reservoir contacted by the injected fluid. The blend of this formulations increases the breakthrough time and improves the sweep efficiency due to the generated foam by CO_2 in contact with surfactant solution. The generated foam increases the injected gas viscosity and increases the contact time of gas and crude oil.

Foam/crude oil interaction (core sample B)

The same displacement process was performed in core sample B. The gas mobility reduction was observed during
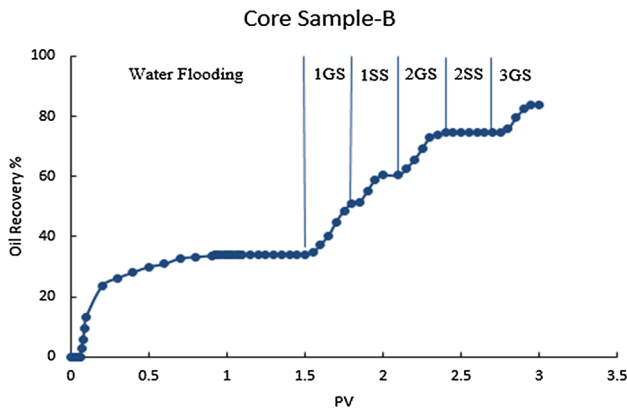
Fig. 6 Oil recovery by surfactant blend of 0.6% AOS + 0.6% LMDO

slug of CO_2 injection after foam surfactant solution. Figure 5 presents the differential pressure of CO_2 before injection of surfactant and CO_2 cycles of SAG1 and SAG2. The increase in Δp of CO_2 slug after injected surfactant slugs showed strong interaction with crude oil. High-pressure differential values by injected CO_2 slugs in both SAG1 and SAG2 cycles resulted in reduction in gas mobility due to generated foam inside the core. Therefore, sweep efficiency was improved by this surfactant blend formulation.

Figure 6 presents the oil recovery based on OOIP by surfactant blend of 0.6% AOS + 0.6% LMDO. Maximum volume of residual oil was recovered during fist injection of SAG1 cycle. The low oil recovery based on OOIP by this surfactant blend was noted as compared to surfactant blend of sample A. This may be due to its higher IFT values as compared to IFT values of sample A. Another possible reason for increase recovery of residual oil by SAG1 cycle is the contact of injected surfactant solution with CO_2, which disperses the gas phase into the liquid phase. This results in the reduction in microscopic sweep efficiency due to gas bubbles in the liquid phase. Table 8 presents the total oil recovery by surfactant blend of 0.6% AOS + 0.6% LMDO.

Table 8 Oil recovery based on OOIP (0.6% AOS + 0.6% LMDO)

Injection steps	Oil collected (ml)	Cum. RF (%)
Water flooding	3.65	34.15
Gas flooding	1.8	51
Surfactant solution	1	60.34
Gas	1.5	74.34
Surfactant solution	0	74.34
Gas	1	83.7

Foam/crude oil interaction (core sample C)

To compare the result of blended surfactant formulations with single surfactant, one surfactant formulation was performed with same displacement steps. Two cycles of SAG1 and SAG2 with equal slug size of 0.3PV were injected. Differential pressure of SAG1- and SAG2-injected cycles was compared. Figure 7 presents the differential pressure of CO_2 before injection of surfactant and CO_2 cycles of SAG1 and SAG2. Injection of CO_2 slug in the first cycle of SAG1 showed small increase in Δp which is inferred moderately stable foam inside the core. Increase in Δp of CO_2 slug is due to the injected slug of surfactant. Increase in Δp of CO_2 first slug showed gas mobility reduction in the core. Decrease in Δp of second CO_2 slug showed that foam was not generated by injected slug of surfactant solution. This is because high gas saturation or injected CO_2 slug is not completely dispersed into the surfactant solution to form a foam bank inside the core. Therefore, it resulted decrease in Δp.

Figure 8 presents the overall oil recovery by single surfactant 0.6% AOS. Table 9 presents the oil recovery based on OOIP (0.6% AOS). The low oil recovery based on OOIP by surfactant solution of 0.6% AOS is due to its
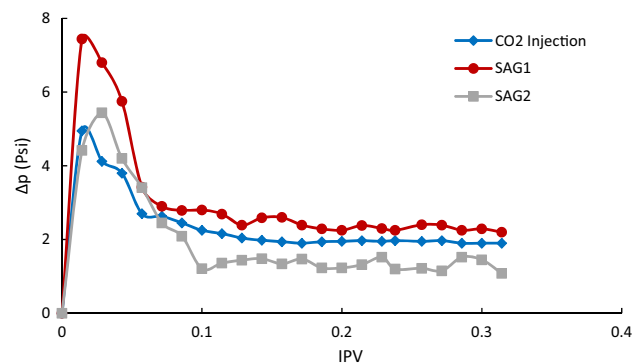

Fig. 7 Δp profile of CO_2 flooding and CO_2 slug of SAG1 and SAG2 injection (0.6% AOS)
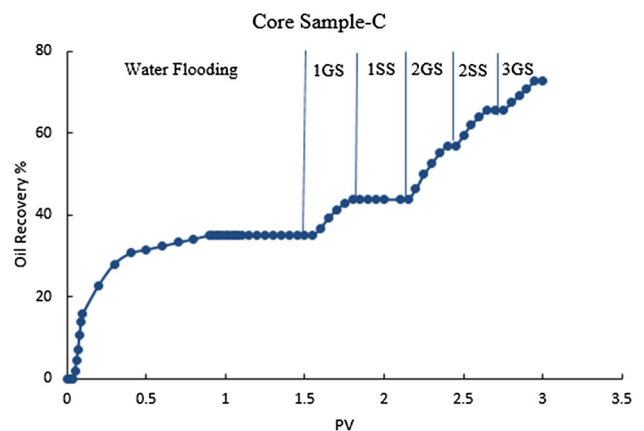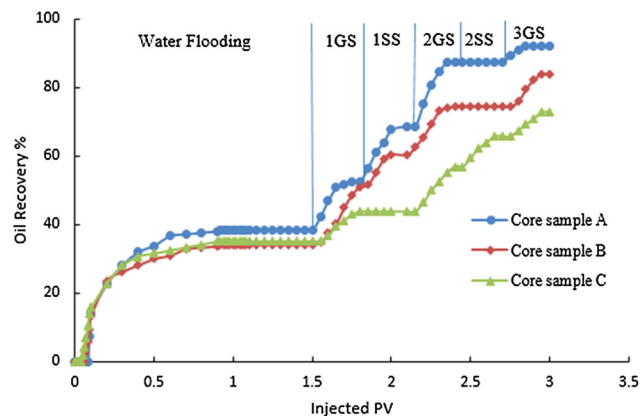

Fig. 8 Overall oil recovery by single surfactant (0.6% AOS)

Table 9 Oil recovery based On OOIP (0.6% AOS)

Injection steps	Oil collected (ml)	RF (%)
Water flooding	4	35.02
Gas flooding	1	43.77
Surfactant solution	0	43.77
Gas	1.5	56.89
Surfactant solution	1	65.66
Gas	0.8	72.66

Fig. 9 Oil recovery based on OOIP by core sample A, B and C

single use in displacement process. This surfactant was not blended with nonionic or amphoteric surfactant.

Effects of new surfactant blend on oil recovery

Figure 9 presents the oil recovery with displacement steps by core sample A, B and C based on OOIP. Maximum oil recovery was by sample A (0.6 wt% AOS + 0.6 wt% TX-100). It was noted as 91.9% OOIP. Sample B (0.6 wt% AOS + 0.6 wt% LMDO) produced 83.7% OOIP. More oil recovery by core sample A is due to its strong interaction with crude oil and low IFT values as compared to core sample B. Core sample C (0.6 wt% AOS) produced 72.66% OOIP. This type of surfactant is not blended and used as a single surfactant. The oil recovery was improved by these surfactant formulations due to sulfonate group presence in the solution. The sulfonate group was stable at 96 °C, making these two surfactant blend formulation as strong candidates for EOR applications.

Conclusions

- Three optimum surfactant formulations were evaluated in the presence of crude oil using Berea sandstone core samples at 96 °C and 1400 psi.

- New surfactant blend formulations can be used and can perform better in the particular range of injection water (34107 ppm) and temperature 96 °C.
- Surfactant blend formulations were reduced IFT values between crude oil and injection water.
- Oil recovery based on original oil-in-place by new surfactant blend formulations of 0.6 wt% AOS + 0.6 wt% TX 100, 0.6 wt% AOS + 0.6 wt% LMDO and individual surfactant of 0.6 wt% AOS were recorded as 91.9, 83.7 and 72.66%, respectively.
- Foam stability in presence of crude oil, reduction in gas mobility and increase in oil recovery indicated that these surfactant blends are good foaming agent as compared to individual surfactant in enhanced oil recovery (EOR) applications.

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