Performance of surfactant blend formulations for controlling gas mobility and foam propagation under reservoir conditions

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Abstract

The use of surfactant is one of the possible solutions to minimize the mobility of gases and improve the sweep efficiency, but the main problem with this process is its stability in the presence of injection water and crude oil under reservoir conditions. In this study, the three types of surfactant anionic, nonionic and amphoteric are examined in the presence of brine salinity at 96 °C and 1400 psia. To access the potential blended surfactant solutions as gas mobility control, laboratory test including aqueous stability, interfacial tension (IFT) and mobility reduction factor (MRF) were performed. The purpose of MRF is to evaluate the blocking effect of selected optimum surfactant solutions. Based on experimental results, no precipitation was observed by testing the surfactant solutions at reservoir temperature of 96 °C. The tested surfactant solutions reduced the IFT between crude oil and brine. The effectiveness and strength of surfactant solutions without crude oil under reservoir conditions were evaluated. A high value of differential pressure demonstrates that the strong foam was generated inside a core that resulted in delay in breakthrough time and reduction in the gas mobility. High mobility reduction factor result was measured by the solution of blended surfactant 0.6%AOS + 0.6%CA406H. Mobility reduction factor of other tested surfactant solutions was found low due to less generated foam by using CO₂ under reservoir conditions. The result of these tested surfactant solutions can provide the better understanding of the mechanisms behind generated foam stability and guideline for their implementation as gas mobility control during the process of surfactant alternating gas injection.

Keywords Foam · Foam quality · Gas mobility · Reservoir condition · Surfactant alternating gas

Introduction

The foam generated by the surfactants has been used in the enhanced oil recovery (EOR) as a gas mobility control. Injection of foam with gas overcomes the problems of viscous fingering, gas channeling and reservoir heterogeneity (Farnazeh and Sohrabi 2013; Green 1998). Trapping of large gas fraction in the reservoir and improving the apparent gas viscosity can significantly reduce the gas mobility (Bernard and Jacobs 1965). The generated foam by different types of surfactants was used in the recent years with several field trials including the flooding of steam foam (Patzek 1996), gas injection alternating with water assisted by foam (Blaker et al. 2002), CO₂ foam flood

(Chou et al. 1992), the foam generated by CO₂ soluble surfactants (Mukherjee et al. 2016), in the fractured fluids (Blauer and Kohlhaas 1974; Wheeler 2010), in the shallow subsurface environmental remediation (Hirasaki et al. 1997; Mamun et al. 2002; Hirasaki 1989), and finally, in the tertiary oil recovery methods to switch the mobility of gas and overcome in situ permeability variations (Blaker et al. 2002). Anionic surfactants such as alpha olefin surfactant (AOS₁₄₋₁₆) are mainly used in the EOR because of their excellent foam stability with a brine composition and tolerant to the presence of crude oil (Cubillos et al. 2012). Sodium dodecyl sulfate (SDS) is an anionic surfactant and used in many cleaning and hygiene products. Ammonium lauryl sulfate or alkyl ethoxy sulfate (STEOL CS-460) is an anionic surfactant with an excellent foaming and foam stability properties. This type of surfactant provides the excellent base for foaming and excellent foaming properties in hard and soft water. Ammonium alcohol ether sulfate (STEPSOL CA-406H) or alcohol ethoxy sulfate (AES) is an anionic surfactant having good foaming properties.

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Internal olefin sulfonate (IOS $C_{15}-C_{18}$) can be used up to 200 °C but has a limited divalent ion tolerance. Alcohol alkoxy sulfate/alkyl ether sulfate (AAS) is used as an additive. This additive has an excellent divalent ion tolerance. Blend with AAS surfactant can improve the salt tolerance (Chemicals 2012). Nonionic surfactants are more tolerant to high salinity, but cannot significantly reduce the interfacial tension (IFT) as compared to the anionic surfactants. Amphoteric surfactants are known as zwitterionic surfactants, are expensive and temperature/brine salinity tolerant. Lauramidopropyl amine oxide (LMDO) is an example. This type of surfactant is used for foam enhancement and viscosity building. Amine oxide can be used as co-solvent with primary surfactant as mixed micelle for EOR. Amine oxides are salt tolerant that reduces the IFT and can develop viscosity. It can be used with anionic, nonionic and cationic surfactants. Sheng et al. (2020) investigated the IFT of anionic–nonionic surfactants and their blended solutions. The experimental result showed that the ethylene oxide (EO) group plays a vital role in the reducing IFT. The hydrophilic–lipophilic balance (HLB) was considered another important factor for reducing the IFT values (Sheng et al. 2020).

The foam can be generated into the reservoir by simultaneous injection of gas and surfactant solutions or alternating injection of gas and surfactant solutions (Xu and Rossen 2003). Surfactant alternating gas (SAG) injection process has several advantages over simultaneous water alternating gas (SWAG) injection process. It minimizes gas–water contact in the surface installations and pipelines, which can be important in the presence of carbon dioxide (Donaldson et al. 1989; Heller 1994; Shi and Rossen 1998). Small slugs of SAG injection can promote foaming in the area near the well bore (Rossen and Gauglitz 1990). The main function of foam injection in the porous media is to control the movement of injected fluids throughout the reservoir with uniform flow. Surfactant concentration and injection velocity are important to control the resistance and the propagation of foam under the field conditions. Foam generated by low surfactant concentration is less stable. Using high surfactant concentration resulted in an increase in apparent viscosity, and improve the sweep efficiency. Understanding of laboratory experiments is considered as important parameter. These studies suggested that all related surfactant parameters must be analyzed before implementing in the field of EOR (Farnazeh and Sohrabi 2013; Al-Mossawy et al. 2011; Talebian et al. 2014). In the field of EOR, three main categories of foam are used.

1. *Pre-formed foam* The pre-formed foam improves higher resistance factor and blocks the porous medium.
2. *Co-injection foam* Co-injection of gas and surfactant solution.

3. *Surfactant alternating gas (SAG) foam* In this injection process, the gas and surfactant solution are injected alternatively. The SAG injection process can be profitable over the co-injection because of easier foam generation. This type of foam cannot block the porous medium completely (Turta and Singhal 1998; Smith 1988; Hansen et al. 1994).

Chang et al. (1994) studied the effects of flow and quality of generated foam. They observed that the mobility of the foam was decreased with increasing flow rate (Chang et al. 1994). The foam generated from the surfactant was first offered by Holbrook for the purpose of controlling gas mobility (Boud and Holbrook 1958). Wang et al. (2017) performed laboratory experiments on four surfactants named nonionic surfactant nonylphenol polyethoxylate (NP), alkyl poly glycoside (APG-1214), anionic surfactant SDS and sodium dodecyl benzene sulfonate (SDBS) for their stability and half-lifetime. They concluded that good performance in the foam stability was obtained by nonionic surfactant (APG-1214) as compared to the other tested surfactants in their study. Further, they used core flood experiments for measuring the resistance factor. Surfactant (AP-1214) resulted in good synergistic when blended with another anionic surfactants (Wang et al. 2017).

Norouzi et al. (2018) studied the potential of foam on oil recovery. The foam propagation and potential of oil recovery by SDS and AOS were performed in the laboratory under pressure of 2000 psia and 65 °C. After water flooding, the co-injection of nitrogen gas (N_2) and SDS was continued with the injection rate of 6 cm³/hour. Similarly, in the second experiment, N_2 gas and AOS were injected alternately with the same injection rate. The maximum foam stability was obtained from both types of surfactant solution. The generated foam stability by SDS resulted in a more stable than generated foam by AOS (Norouzi et al. 2018). Zhang et al. (2020) investigated the amine surfactants for smart mobility control during the CO₂ flooding. They concluded in their experimental results that the tested amine surfactants performed better CO₂ foaming ability under high temperature and high pressure (Zhang et al. 2020). It is clear from the previous studies, lot of research have been performed on foam stability, which was generated by different types of surfactants followed by CO₂ injection. The generated foam acts as gas mobility control that results in improving the overall sweep efficiency. Most of the laboratory experiments were performed on different types of individual and blended surfactant solutions with low to high concentration. The focus was given on performed testing in terms of their generated foam stability, longevity and other parameters that effect the generated foam stability (Farzaneh and Sohrabi 2015; Simjoo et al. 2013; Memon et al. 2016). Extensive laboratory work has been done to study the performance

Table 1 List of surfactants used in the experiments

S. no.	Chemical name	Chemical description	Surfactant type	Active percent
1	BIO-TERGE AS-40 AOS _{C14–16}	Alpha Olefin sulfonate	Anionic	39
2	STEPSOL CA-406H	Ammonium alcohol ether sulfate	Anionic	60
3	ENORDET 0332 (IOS _{C15–18})	Internal olefin sulfonate	Anionic	33.4
4	SDS	Sodium dodecyl sulfate (solid)	Anionic	100
5	Triton TX-100	Octylphenol ethylene oxide	Nonionic	100
6	ENORDET J771 (AAS)	Alcohol alkoxy sulfate/alkyl ether sulfate	Additive	26.2
7	STEOL CS-460	Sodium lauryl sulfate, 3MolesEO	Secondary Surfactant	59
8	AMMONYX LMDO	Lauryl amido propyl amine oxide	Amphoteric	33

of foam in the conventional and unconventional reservoirs (Szlendak et al. 2013; Yang et al. 2019; Das et al. 2016). However, the selection of surfactant under particular reservoir condition is important. In this research study, the experiments have been accomplished in order to examine the mechanism of foam generated by using single and solution of blended surfactants under reservoir conditions. The purpose is to check the effectiveness and strength of optimum surfactant solutions without crude oil under reservoir conditions and the flowing behavior of different surfactant blended solutions with different concentrations through porous media. The blocking effect by surfactants on porous media was investigated. Foam generated from surfactants, either single or blended solutions, improved the volumetric sweep efficiency, reduced the gas mobility that resulted in a favorable mobility ratio. The findings of this research study on blended surfactants are favorable for gas mobility control during the SAG applications.

Materials

Surfactants

In the experiment, surfactants were used as received without further treatment. For the preparation of stock solution, 5% of each surfactant was used in distilled water. From prepared stock solution, required concentration of each surfactant solution was mixed with prepared injection water. Table 1 shows the list of commercial surfactants used in this study.

Synthetic brine (injection water)

Injection water is prepared in the laboratory according to the field formation water. Table 2 shows the salts used in the injection water.

Table 2 Salts used in the prepared injection water

Salt	g/l
NaCl	23.6
CaCl ₂ ·2H ₂ O	1.3
MgCl ₂ ·6H ₂ O	10.20
KCl	0.62
NaHCO ₃	0.225
Na ₂ SO ₄	3.9

Table 3 Crude oil properties

Oil type	Waxy crude oil
Viscosity (Cp) 96 °C, 1400 psia	1.5
Density (g/cm ³) 96 °C, 1400 psia	0.7886
⁰ API	37.7
Wax content (%)	26.7
Saturates (%)	82.15
Aromatics (%)	15.4
Resins (%)	2.26
Asphaltenes (%)	0.18

Crude oil

Malaysian crude oil was used for this research study. The properties of this crude oil are shown in Table 3.

CO₂ gas

CO₂ gas with purity of 99.9% was used in the core flood experiment under 1400 psia and 96 °C. Table 4 shows the properties of pure CO₂ gas.

Table 4 Properties of CO₂ gas

Properties	Result
Apparent molecular weight (g/mol)	44
Density of CO ₂ (g/cm ³)	0.1854
Viscosity of CO ₂ (cp)	0.0184
Critical temperature (°C)	31.1
Critical pressure (psia)	1070

Table 5 Chemical composition of Berea sandstone

Chemical composition	Percentage (%)
Silica (SiO ₂)	93.13
Alumina (Al ₂ O ₃)	3.86
Magnesium oxide (MgO)	0.25
Ferric oxide (Fe ₂ O ₃)	0.11
Ferrous oxide (FeO)	0.54
Calcium oxide (CaO)	0.10

Table 6 Berea sandstone core properties

Sample ID	Diameter (cm)	Length (cm)	Pore volume (cm ³)	Bulk volume (cm ³)	Porosity (%)	Liquid permeability (mD)
M1	3.827	7.658	18.46	88.04	20.9	153.5
M2	3.860	7.625	17.49	89.18	19.6	153.5
M3	3.855	7.632	17.42	89.03	19.57	172
M4	3.863	7.663	17.54	89.76	19.54	145.2
M5	3.830	7.668	17.70	88.29	20	164
M6	3.853	7.653	18.17	89.18	20.37	149

Berea sandstone

Table 5 shows the chemical composition of Berea core samples and Table 6 shows the Berea sandstone core properties (Berea sandstone 2014). The digital caliper was used to measure the length and diameter of core samples and the measurement was taken accurately on the LCD screen.

Methodology

Interfacial tension

A spinning drop tensiometer (Model SV T20) was used to measure the IFT values of crude oil/brine water and crude oil/surfactant solutions at atmospheric pressure and constant temperature of 85 °C. Temperature 85 °C was used due to the transparent visualization of crude oil drop in the capillary tube. At 96 °C, oil drop cannot be seen due to the creation of vapors in aqueous mixed surfactant solution.

Figure 1 shows the experiment performed on SV T20 spinning drop tensiometer. The cleaned capillary tube is filled with the surfactant-containing brine solution. After that, the drop of crude oil is injected inside the capillary tube by using syringe. The injected drop size was observed as three times greater in diameter than minor diameter drop. This is compulsory for accurate IFT measurements. The rotating speed of capillary tube was steadily increased in order to elongate the oil drop and to make it an elliptical shape. After attainment of the elliptical shape of oil drop, a dimensional profile was extracted and then hold down to initiate the IFT measurement.

Core flood experiment

Core flood equipment was used for SAG experiments. The schematic flow diagram of fluid displacement process during the experiment is shown in Fig. 2. The core flood equipment consists of a core holder, ISCO syringe type pumps for controlling the confining and back pressure during the

Fig. 1 Elliptical shape of oil drop during experiment by SV T20 spinning drop tensiometer

fluid displacement process. The pump was connected with three stainless steel accumulators, where the test fluid can be stored and circulate to the core. All operating valves, piping

Fig. 2 Schematic diagram of SAG flooding

and transmitters are made in acid-resistant material to protect the corrosion. For each experiment test, a separate Berea sandstone core sample was used. The core samples were vacuumed and saturated with brine water for 3 days. The core was placed in the Hassler core holder horizontally. Air was used as confining fluid. The back pressure regulator (BPR) is connected to exit of core that was also controlled by the pump. The brine water, CO₂ and surfactant solutions were transferred into the three accumulators that were set in the oven. Core holder was set in an oven under test temperature of 96 °C and back pressure of 1400 psia. The confining pressure was set at 1900 psia. The injection water was injected with fixed rate of 0.50 cm³/min. After that, the prepared optimum solution of blended surfactant was injected before and after injection of CO₂ slug with the same injection rate. Each fluid was injected until the steady-state condition. The fluid (effluent) was collected in the graduate glass cylinder.

Results and discussion

The aqueous stability of selected surfactant solutions in the presence of brine salinity was evaluated at 96 °C. The compatibility of these surfactants is monitored over time up to 4 weeks by observing the aqueous stability in terms of no phase separation, clouds and precipitation.

The MRF is calculated through the differential pressure profile by using the core flood experiments described in the previous published work (Memon et al. 2016). It was concluded in our published work that the blended surfactant solution with equal concentration of 0.6 wt%AOS + 0.6 wt%TX100 and 0.6 wt%AOS + 0.6 wt%LMDO performed better under

reservoir conditions as compared to the single surfactant solution of 0.6 wt%AOS. In this study, further six surfactant solutions were tested for gas mobility control at the fixed injection rate under the same reservoir conditions (96 °C and 1400 psia).

Interfacial tension

The IFT values between crude oil/brine water are measured with tensiometer at 85 °C resulted in 12 mN/m. The IFT values between crude oil/surfactant solutions are reduced from 12 to 1.85 mN/m. Table 7 shows the measured IFT values of all surfactant solutions. Low IFT values were achieved by using blend of surfactants with different concentrations. The reduction of IFT values from all different concentrations is due to the surfactant molecules adsorbed at the interface and provided the expanding force acting against the normal IFT. Therefore, all concentrations of AOS_{C14–16} and its blend moved to the lower IFT. The IFT between surfactant SDS/oil and its blend with other surfactant solution was tested with crude oil. The same trend of reduction in IFT was obtained with increase in the concentrations of surfactants.

Table 7 Interfacial tension of tested surfactant solution

Core ID	Formulations	IFT (mN/m)
M1	0.2%AOS + 0.2%TX-100/oil	0.92
M2	0.6%AOS + 0.6%CS460/oil	1.32
M3	0.6%AOS + 0.6%CA406H/oil	1.85
M4	0.2%SDS + 0.2%TX-100/oil	1.5
M5	0.4%SDS + 0.4%AAS/oil	1.15
M6	0.4%IOS _{C15–18} /oil	0.134

An increase in IFT value was observed by surfactant blend of 0.6%AOS + 0.6%CA406H/oil as compared to the other surfactant solutions. The general trend is that IFT value is decreased with increasing of surfactant concentrations. The increase in IFT value is due to high dissimilarity into two phases at the interface, or due to the Gibbs–Marangoni elasticity effect. As the film stretches under an applied stress, the area was increased and amount of surfactant adsorbed at the gas/liquid surfaces. Gibbs elasticity increases with an increase in surfactant concentration (Acharya et al. 2005). Therefore, the tested surfactant solutions reduced the IFT between crude oil and brine. Low IFT is a result of strong interactions between surfactant and oil molecules.

Mobility reduction factor

Equation 1 is used for calculating the MRF values, which were suggested in the published papers (Hirasaki et al. 1997; Mannhardt et al. 2000; Schramm 1994; Rosman and Kam 2009). Mathematically:

$$\text{MRF} = \frac{\Delta p(\text{presence of surface tan } t)}{\Delta p(\text{without surface tan } t)} = \frac{\Delta p_{\text{Foam}}}{\Delta p_{\text{no Foam}}}. \quad (1)$$

The generated foam by the surfactant solution M1 (0.2%AOS + 0.2%TX100) with equal concentration in the presence of CO₂ at 1400 psia and 96 °C is shown in Fig. 3. An increase in the pressure was detected when another slug of CO₂ was injected after the injection of surfactant solution. In this displacement process, less foam was generated inside a core sample to control the gas mobility. The use of low concentration of this surfactant blend showed small values of MRF. The blended surfactant solution 0.6 wt%AOS + 0.6 wt%TX100 used in the previous study showed good reduction in the gas mobility due to the stable foam inside a core (Memon et al. 2016). Therefore, the maximum foam stability can provide better reduction in the

Fig. 3 Performance of injected CO₂ slug before and after blended surfactant solution of 0.2%AOS + 0.2%TX100

gas mobility. Figure 4 shows the differential pressure and MRF of M2 (0.6%AOS + 0.6%CS460) core sample. Differential pressure profile showed that less foam was generated at the initial displacement of this surfactant blend. The strong foam was generated after injecting 1.7 pore volume of CO₂ injection. Therefore, the generated foam by this type of surfactant blend is considered from weak to strong foam. The differential pressure of M3 (0.6%AOS + 0.6%CA406H) core sample is shown in Fig. 5. Same behavior in differential pressure was recorded as surfactant blend solution used in core M2. Constant MRF was not observed by this type of surfactant blend because differential pressure was not reached at steady-state conditions. At the first stage, after injected 1.15PV of CO₂ differential pressure showed that rise in the MRF values. The differential pressure increased dramatically up to 80 psia. This increase in the differential pressure was due to the foam generated inside a core and maintained high apparent viscosity. The differential pressure starts to decline after 2.2PV gas injected. Small reduction in gas mobility was observed by this surfactant blend solution. The differential pressure of M4 (0.2%SDS + 0.2%TX-100) core sample versus pore volume is shown in Fig. 6. Same performance was observed during the displacement process

Fig. 4 Performance of injected CO₂ slug before and after blended surfactant solution of 0.6%AOS + 0.6%CS460

Fig. 5 Performance of injected CO₂ slug before and after blended surfactant solution of 0.6%AOS + 0.6%CA406H

Fig. 6 Performance of injected CO₂ slug before and after blended surfactant solution of 0.2%SDS + 0.2%TX100

Fig. 7 Performance of injected CO₂ slug before and after blended surfactant solution of 0.4%SDS + 0.4%AAS

as the surfactant blend (0.2%AOS + 0.2%TX100) performed in the core sample M1. Less foam was generated inside a core sample by this surfactant blend solution to reduce the gas mobility. Figure 7 shows the differential pressure of M5 (0.4%SDS + 0.4%AAS) core sample. Increase in pressure differential was observed continuously after injecting one pore volume (1PV). Addition of additives AAS to surfactant solution of SDS can produce the synergistic effect, that increase the stability of generated foam by improving the lamellae elasticity, strengthening the lamellae to decrease the gas diffusion, dropping the liquid drainage and increasing the viscosity of tested surfactant solution. The foam made by this blend of surfactant is considered more constant as compared to the blended surfactant solution of M4 (0.2%SDS + 0.2%TX100). Figure 8 shows the differential pressure of M6 (0.4%IOSC_{15–18}) core sample. Weak foam was observed through pressure differential profile by this type of surfactant. The decline in the differential pressure showed early breakthrough, which resulted from the density and viscosity difference between the two injected fluids. The single surfactant with concentration of 0.4%IOSC_{15–18} was generated less amount of foam and was less stable. The less foam stability by this surfactant IOSC_{15–18} was

Fig. 8 Performance of injected CO₂ slug before and after single surfactant of 0.4%IOSC_{15–18}

Table 8 MRF result of surfactant formulations at reservoir conditions

Core ID	Formulations	$\Delta p_{(no\ foam)}$	$\Delta p_{(foam)}$	MRF
M1	0.2%AOS + 0.2%TX-100	6.23	10.73	1.72
M2	0.6%AOS + 0.6%CS460	24.79	43.18	1.74
M3	0.6%AOS + 0.6%CA406H	18.48	43.8	2.37
M4	0.2%SDS + 0.2%TX-100	20	29.15	1.46
M5	0.4%SDS + 0.4%AAS	29.18	43.96	1.51
M6	0.4%IOSC _{15–18}	15.4	17.13	1.11

due to their large specific surface area per unit of molecules (Kumar and Mandal 2016, 2017). Due to the large size and nonionic nature of the IOSC_{15–18} surfactant head group, its Gibbs–Marangoni effect is weak. Consequently, more rapid degradation of the foam was observed. Also the performance of generated foam by using CO₂ depends on the selected surfactant characteristics and required parameters such as injection water salinity, pressure and temperature. The density of CO₂ increased under high pressure, while the impact of pressure on the density of water was negligible. Therefore, it was clear that the change in pressure can alter the hydrophobicity and hydrophilicity of the surfactant. The solubility of gas in water has a negative effect on the stability of the foam generated because it can accelerate the coalescence of the generated foam. Table 8 shows the differential pressure and MRF of evaluated individual and blended surfactants under reservoir conditions at fixed injection rate of 0.50 cm³/min. The mobility reduction through core displacement experiment was the result of surfactant type, its concentration and injection rate. Generally, gas mobility was reduced when generated foam must be stable under the reservoir conditions. High MRF values were obtained by the solution of blended surfactant 0.6%AOS + 0.6%CA406H. An increase in the MRF values by this blend surfactant showed that the generated foam was stable. The decline in the stability of generated foam due to the presence of

salinity, high temperature and other parameters has led to chemical modifications and formulations with the development of new technologies (Mannhardt et al. 2000; Zhu et al. 1998). Obtained MRF values larger than one indicated that the foam was generated inside a core. If the value of MRF is lower than one ($MRF < 1$), this means that there is no foam generated inside the core. MRF range is considered as 1–10,000 (Sheng 2013), when foam becomes stable, more resistance to flow, that resulted in a higher mobility reduction. The MRF result showed that the blended surfactants exhibited better foam stability than the foam generated by using individual/single surfactant.

Conclusions

- The effectiveness and strength of a single surfactant and five blended surfactant solutions in the absence of oil under reservoir conditions were evaluated at fixed SAG injection rate.
- Surfactant AOS_{C14–16} was recognized as good foaming agent in SAG. Good stability was observed when AOS_{C14–16} was blended with other surfactant solutions. These blended surfactant solutions reduced the IFT between crude oil and brine.
- A high value of differential pressure indicated that the generation of strong foam inside a core resulted in delay in breakthrough time and reduction in the gas mobility.
- Maximum MRF result was obtained by a blend of surfactant solution 0.6%AOS + 0.6%CA406H at the reservoir pressure of 1400 psia and temperature 96 °C.
- The solution of blended surfactants plays an imperative role in controlling the mobility of gas during the alternating injection of surfactant and gas.

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