Investigation of the Effect of Nanoparticle-Stabilized Foam on EOR: Nitrogen Foam and Methane Foam
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ABSTRACT: In recent years, studies conducted on foam stabilization have focused on nanoparticles by generating strong adsorption at the interface to stabilize the foam under harsh reservoir conditions. Meanwhile, the selection of a gas source is also of great importance for foam performance. In this study, a mixed system of surfactants was selected, and the foamability and foam stability of nitrogen and methane were evaluated according to the improved jet method. After adding modified SiO2 nanoparticles, the foam-related parameters were analyzed. The plugging abilities of the different foams were compared through core-flooding experiments, and the oil displacement effects of the different foams were compared through microfluidic experiments. The results show that the amphoteric surfactant betaine has an excellent synergistic effect on the anionic surfactant SDS. The methane foam produced using the jet method has a larger initial volume than the nitrogen foam, but its stability is poor. The half-life of the nitrogen foam is about two times that of the methane foam. After adding 1.0 wt % SiO2 nanoparticles to the surfactant solution, the viscosity and stability of the formed foam improve. However, the maximum viscosity of the surfactant nanoparticle foam (surfactant-NP foam) is 53 mPa·s higher than that of the surfactant foam. In the core-flooding experiment, the plugging performance of the methane foam was worse than that of the nitrogen foam, and in the microfluidic experiment, the oil displacement abilities of the methane foam and the nitrogen foam were similar. The plugging performance and the oil displacement effect of the foam are greatly improved by adding nanoparticles. The surfactant-NP foam flooding has a better oil displacement effect and can enhance the recovery factor by more than 30%. Under actual high-pressure reservoir conditions, although the stability of the methane foam is weaker than that of the nitrogen foam, some methane may be dissolved in the crude oil to decrease the viscosity after the foam collapses, which leads to the methane foam being the preferred method in oilfields.

1. INTRODUCTION
With the gradual maturity of gas preparation technology, gas flooding has become a widely used method for enhancing oil recovery in oilfields.1 According to statistics, the contribution of gas flooding to global oil production has increased, accounting for 38.4% (onshore oilfields) and 68.4% (offshore oilfields) of the total production.2 During gas flooding, viscous fingering and gas channeling caused by an unfavorable gas–oil mobility ratio are the main problems leading to the reduction of the recovery factor. The common methods used for preventing gas channeling include water-alternating-gas (WAG) injection, simultaneous water-alternating-gas (SWAG) injection, and surfactant-alternating-gas (SAG) injection. The formation of foam is very likely to occur during SAG injection. Foam improves the flooding efficiency by increasing the sweep coefficient and reducing the gas mobility during the gas injection process, which has promoted the development of foam flooding enhanced oil recovery (EOR) technology.3–5

The main factors affecting the EOR of foam flooding are the stability and plugging performance of the foam system.6,7 There are many challenges in the generation and stabilization of foam under reservoir conditions. The harsh conditions, such as the reservoir temperature, salinity, and rock adsorption of surfactants, may lead to poor foam formation and directly affect the sweep efficiency during the displacement process. The foam must be stable enough to function effectively, and
The use of nanoparticles has replaced the use of surfactants to a certain extent. The generation of strong adsorption at the interface to stabilize the foam under harsh reservoir conditions has been extensively studied. In recent years, SiO₂ nanoparticles have been the focus of foam stabilization research. Because SiO₂ is rich in natural materials, it is generally considered to be an environmentally friendly additive. Untreated SiO₂ nanoparticles exhibit hydrophobicity. For the foam stabilization mechanism of hydrophilic nanoparticles, Horozov et al. proposed three hypotheses. After the hydrophilic particles penetrate the liquid film, they act as a single layer of bridging particles and as a tightly packed double layer of particles, and the particles aggregate into a network inside the film. Kim et al. used nonionic surfactants to test the foam-stabilizing properties of different SiO₂ nanoparticles. They found that smaller particles produce more stable foam due to the larger diffusivity and higher interface of smaller nanoparticles. One of the disadvantages of SiO₂ nanoparticles is that they are negatively charged on the surface, which hinders the regulation of hydrophobicity. Several scholars have reported synergistically stabilizing foams produced by mixing surface-modified SiO₂ nanoparticles and anionic surfactants. Sun et al. introduced modified hydrophobic SiO₂ nanoparticles into the foam system and studied the synergistic foam stabilization mechanism with surfactants and the rheological properties of the gas-liquid interface. They found that the surfactant molecules were adsorbed onto the particle surfaces at an appropriate concentration. After that, the surface activity of the particles can be enhanced, which helps the particles adsorb at the gas-liquid interface and changes the structure of the interface layer of the particles, thereby enhancing the expansion viscoelastic modulus and the stability of the foam.

Although many studies have been conducted on nanoparticle-stabilized foam, the choice and application of the gas source are key to implementation of foam technology. Air, CO₂, and N₂ have mainly been used in indoor research. However, for China’s partial reservoirs, nitrogen foam flooding is still the main method due to the maturation of nitrogen preparation technology. Although air foam is convenient, due to its high oxygen content, it often causes corrosion of the downhole tubular strings. For CO₂ foam flooding, its oil displacement effect in oilfields is good, but because of the scarcity and cost of CO₂ gas sources in certain areas, its application has been restricted. The distribution of natural gas in China is uneven, and there are abundant natural gas sources in certain oil reservoirs in the west. When natural gas is dissolved in crude oil, the viscosity of the crude oil decreases. After solving production safety problems, natural gas foam flooding can be used. However, although there are many field applications of natural gas flooding, research on the natural gas foam and methane foam is still scarce.

In this study, the properties and applications of the methane foam were evaluated and compared with the widely used nitrogen foam, and the performance changes of the two foams after adding nanoparticles were compared. First, the jet method was used to evaluate the formation and static stability of the nitrogen foam and methane foam for three types of surfactants. After determining the surfactant type, the interaction between the nanoparticles and the surfactant was investigated, and the foam-related parameters, such as the interfacial tension, viscoelastic modulus, and apparent viscosity, were evaluated. Furthermore, core-flooding experiments were carried out to compare the plugging performances of the nitrogen foam and methane foam with and without the addition of nanoparticles, and the dynamic changes in the produced foam were monitored. Finally, the oil displacement effect of the four foams was evaluated, and the mechanism of increasing the oil displacement capacity of the methane foam after adding nanoparticles was clarified. In addition, the advantages of the methane foam are proposed. The results of this study provide guidance for the application of natural gas foam and have important theoretical and practical values for the application of natural gas foam flooding technology in oil and gas field development.

2. MATERIALS AND METHODS

2.1. Materials. 2.1.1. Chemicals. The foaming agents used include anionic surfactants sodium dodecyl sulfate (SDS) and aerosol-OT (AOT), a nonionic surfactant lauryl alcohol polyoxyethylene ether (C₁₂E₂₃), and an amphoteric surfactant betaine. Ethanol-stabilized nanoparticles were used for particle size measurement, bromocresol green and naphthalene ethylenediamine were mixed in a certain proportion to stain the foam, and eosin was used to stain the brine. All of these chemicals are purchased from MClean Technologies Pte., Ltd., Singapore, and have a purity of more than 99.0%.

The modified hydrophobic SiO₂ nanoparticles (provided by Wacker Chemicals Co., Ltd., Germany, product code HDK H18) have an average particle size of about 20 nm, purity greater than 99.8%, and a mass loss after drying at 105 °C for 2 h of less than 0.6 wt %. The specific surface area measured using the Brunauer–Emmett–Teller (BET) method is 200 ± 30 m²/g. The surface modification material is dichlorodimethylsilane, the density of the silanol groups on the surface is less than 0.5, and the contact angle of the aqueous phase is 122.21°. Figure 1 shows a transmission electron microscopy (TEM) image of the H18-type SiO₂ nanoparticles.

Figure 1. TEM image of the H18 SiO₂ nanoparticles.

2.1.2. Gases. Methane (CH₄) with a purity of 99.99% and nitrogen (N₂) with a purity of 99.99% were purchased from Qingdao Tianyuan Co., Ltd., China. It should be noted that CH₄ must be prevented from leaking during use and N₂ was used to conduct leakage tests prior to the sandpack tests.

2.1.3. Sandpack Model. One cylindrical sandstone sandpack model with a length of 30.00 cm and an inner...
diameter of 2.54 cm was prepared to simulate the physical porous media used in the sandpack flooding tests. The detailed averages of the sandpack model parameters are as follows: the porosity is 41.45% and the permeability is 2894 mD.

2.1.4. Oil. Crude oil from the Jidong oilfield was used in the oil recovery experiment, and its properties are listed in Table 1.

| Specification                        | Crude Oil |
|--------------------------------------|-----------|
| Oil density at 50 °C (kg·m⁻³)       | 775.2     |
| Oil viscosity at 25 °C (mPa·s)       | 340       |
| Oil viscosity at 50 °C (mPa·s)       | 20        |
| Saturates (wt %)                     | 70.06     |
| Aromatics (wt %)                     | 19.65     |
| Resins (wt %)                        | 9.69      |
| Asphaltenes (wt %)                   | 0.60      |

“SARA”—saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes.

2.2. Methods. 2.2.1. Foaming Agent Preparation. The anionic surfactant SDS was mainly used, and the other three types of surfactants were mixed in a 3:1 ratio. The compositions of the surfactant used in the foaming agent screening stage were 0.15% SDS + 0.05 wt % AOT (denoted S-A), 0.15% SDS + 0.05 wt % C₁₂E₂₃ (denoted S-C), and 0.15% SDS + 0.05 wt % betaine (denoted S-B).

The preparation process of adding nanoparticles to the foaming agent is as follows. (1) Weigh a certain amount of SiO₂ nanoparticles and dissolve it in ethanol (the mass ratio of ethanol to particles is 9:1). (2) Stir thoroughly with a glass rod, pour the mixture into an appropriate amount of deionized water, and then disperse it for 10 min using ultrasound. (3) Divide the mixture into even parts after sonication and put the parts into a centrifuge. Repeat the centrifugal operation of adding water to remove the defoaming ethanol. (centrifuge at 150 rpm for 15 min and repeat four times). (4) After centrifugation, pour the contents of each centrifuge tube into a beaker, ultrasonically disperse it for 1 h, and then magnetically stir the mixture for 6 h to prepare a hydrophobic nanoparticle dispersion. Dilute the dispersion to obtain a series of lower concentrations. (5) Mix the prepared nanoparticle dispersions with the foaming agent in the specified proportions and magnetically stir at a low speed for 6 h to prepare a foaming agent/hydrophobic nanoparticle compounding system.

2.2.2. Foam Formation and Stability. We used the improved jet method²⁶ based on the Ross–Miles method to generate the foam. The specific process is shown in Figure 2. The steps are as follows. (1) Fill the measuring cylinder with water and plug it with a rubber stopper with two small holes. Connect the measuring cylinder to the outside using a pipeline with a control switch valve at the small hole. The internal volume of the measuring cylinder is 70.5 mL. (2) Close the valves of the two sections of the pipeline plugged with rubber stoppers and place the measuring cylinder upside down in a thermostatic water tank. When the water surface is slightly past the rubber stoppers, open the valves to communicate with the gas source. Because nitrogen/methane is difficult to dissolve in water, dewatering gas production occurs in the measuring cylinder. Finally, a cylinder filled with gas is obtained, and the valve is closed. (3) After placing the measuring cylinder upright, quickly open the valve and inject 23.5 mL of foaming agent into the measuring cylinder using a syringe (within 3 s). Close the valve when finished. (4) Place the measuring cylinder in a constant-temperature water tank, monitor the change in the foam volume with time, and check the tightness of the measuring cylinder in the constant-temperature water tank.

2.2.3. Interfacial Tension and Viscoelastic Modulus Measurements. The interfacial tensions and viscoelastic moduli of the solutions and dispersions at 25 °C were measured using the Tracker-H instrument (Teclis, France, a full scale of 20.0 MPa and 200 °C) and the pendant drop method. During the measurements, the oscillation period was 5 s, the oscillation frequency was 0.2 Hz, and the amplitude was 10%. The gas was passed into a closed kettle with a pressure of 0.1 MPa, and then, the syringe containing the liquid to be measured was adjusted to form a pear-shaped bubble. The bubble’s shape was input into a computer using a charge-coupled device (CCD) camera. The interfacial tension was calculated based on the shape of the bubble and the Laplace equation, and the interfacial viscoelastic modulus was obtained by processing the experimental data using a Fourier transform. The formula for calculating the viscoelastic modulus is

\[
E = \frac{d\gamma}{d \ln A}
\]

where \(\gamma\) is the interfacial tension (mM/m), \(A\) is the surface area of the bubble (m²), and \(E\) is the viscoelastic modulus (mN/m).

2.2.4. Apparent Viscosity of the Dispersions. The viscosities of the foaming agent and foam were measured using a concentric barrel model and an MCR 302 rheometer (Anton Paar, Austria, a full scale of 15.0 MPa and 300 °C).
The shear rate was fixed at 100 s\(^{-1}\), and the temperature was maintained at 25 °C.

2.2.5. Microstructure of the Foam. The foam produced by the foam generator was collected on a glass slide and placed on a VHX-5000 super-depth-of-field 3D microscope (Keyence, Japan) at room temperature (25 °C) for observations. The foam’s drainage process and the changes in the foam’s microstructure were recorded.

2.2.6. Foam Blocking Experiment. The experimental procedure is shown in Figure 3. Two high-pressure transfer vessels were used to hold the surfactant solution and water. The vessels were driven by a 100 DX high-pressure piston ISCO pump (Teledyne Technologies). In the water flooding stage, the water injection rate into the sandpack was 3 mL/min. In the foam flooding stage, the surfactant injection rate was 1 mL/min. The N\(_2\) or CH\(_4\) gas source injection rate was maintained at 2 mL/min by a gas flowmeter. The gas and liquid were mixed in the foam generator to produce foam, which was then injected into the sandpack. A backpressure valve was installed at the end of the sandpack model to maintain the system at the desired pressure (1.2 MPa). During the displacement process, the pressure on both sides of the sandpack was continuously monitored using digital pressure sensors and recorded by a data acquisition system connected to a computer. The fluid produced was collected at the exit for analysis.

Initially, the sand filling tube model was filled with dry 80−100 mesh quartz sand. During the filling process, it was compacted while vibrating to ensure the compactness and homogeneity of the porous medium. Thereafter, the porosity of the sandpack model was measured using brine water after vacuuming. The volume of the imbibed water was considered to be the pore volume (PV) of the model. The ratio of the pore volume to the model volume was used to calculate the porosity of the model. After the model was saturated with water, the water was continuously injected at a rate of 10 mL/min using a pump, and the pressure difference after reaching the steady state was recorded. The absolute permeability of the model was calculated using Darcy’s formula.

2.2.7. Oil Recovery Experiment. To more intuitively understand the microscopic process of foam flooding, a microfluidic experiment was performed using a micro glass model. Similar devices and methods have been introduced in previous studies.\(^{27}\) The experimental device and process used in the oil recovery experiment are similar to those used in the oil-free foam plugging experiment. However, a high-pressure transfer vessel for the crude oil was added, and the sandpack was saturated with oil at a low flow rate using a pump to calculate its initial oil saturation. Similar to the displacement process shown in Figure 3, the water injection rate was changed to 0.015 mL/min in the water flooding stage. In the foam flooding stage, the rate of surfactant injection was changed to 0.005 mL/min, and the rate of gas injection was changed to 0.01 mL/min.

### 3. RESULTS AND DISCUSSION

#### 3.1. Foamability and Foam Stability of Nitrogen and Methane. The foam volume and foam half-life tests were performed using three types of surfactants and two sources (nitrogen and methane). Figures 4 and 5 show a comparison of

![Figure 3. Schematic of the foam flooding experiments in the sandpack system.](image)

![Figure 4. Foam volume comparison of the different surfactant formulation systems.](image)
for the produced methane foams, the anionic--amphoteric surfactant S-B has the best foaming performance. Regardless of the type of surfactants, the initial volume of the nitrogen foam produced is smaller than that of the methane foam. From Figure 5, it can be seen that in terms of foam half-life, the stability of the foam produced by surfactant S-A is the worst, and the stability of the foam produced by surfactant S-B is far greater than those of the other two. The stabilities of the three surfactants corresponding to the nitrogen foam are better than those of corresponding to the methane foam, and the half-life of the nitrogen foam is about twice that of the methane foam.

Based on the interfacial tension and viscoelastic modulus tests between the gas and three surfactants, the interfacial tension between the methane gas and the surfactant is smaller than that between nitrogen and the surfactant, and the viscoelastic modulus of the active droplets filled with methane gas is larger than that filled with nitrogen. This explains why the initial volume of the methane foam is larger than that of the nitrogen foam. Under the same conditions, the solubility of nitrogen in water is less than that of methane, which results in the liquid drainage rate of the nitrogen foam being less than that of the methane foam, so the nitrogen foam has better stability. Finally, surfactant S-B was selected. The amphoteric surfactant was compatible with the other types of surfactants, especially those capable of accepting a proton, and it may also exhibit synergy with the anionic surfactant through electrostatic interactions. This further decreases the interfacial tension. In both a nitrogen and methane atmosphere, it has the lowest interfacial tension, the highest viscoelastic modulus, and good foamability and foam stability, and the foam volumes of the different gas sources are significantly different.

Different concentrations of S-B were placed in a nitrogen and methane atmosphere, respectively, and the interfacial tension and viscoelastic modulus were measured. The results are shown in Figure 6. As the S-B concentration increases, the interfacial tension curve shows a linear decrease, and then it approaches a gentle change. The position where the inflection point corresponds to the S-B concentration is around 0.1 wt %, while the viscoelastic modulus curve initially increases and then decreases. The highest point (red star) also corresponds to an S-B concentration of around 0.1 wt %. It is concluded that the critical micelle concentration (CMC) of S-B is around 0.1 wt %, and the surfactant molecules are saturated at the interface. When the concentration is exceeded, the interfacial tension changes slowly or no longer changes. Supersaturation of the surfactant molecules adversely affects the interface, resulting in a low interfacial viscoelastic modulus. As can be seen from Figure 6, the interfacial tension of S-B in methane gas is smaller than that in nitrogen, so less energy is required to form the methane foam. Therefore, S-B has a stronger foaming ability in methane. However, the viscoelastic modulus of S-B in methane is greater than that in nitrogen, and the stability of the formed methane foam is not as good as that of the nitrogen foam. This is due to the different diffusivities of the gases. The methane diffusion rate is faster than the strong foam drainage and foam disproportionation caused by nitrogen.

We also conducted a study on the stability of the foam after it flows through the porous medium. The concentration of surfactant S-B was maintained at 0.1 wt %, and the dyeing treatment was performed. The dosages of naphthalene ethylenediamine hydrochloride and bromocresol green were 0.01–0.03 and 0.04–0.06 wt %, respectively. The same injection conditions were set, only the gas source was changed, and the produced foam was collected in a transparent glass sampling bottle. After being filled with foam, the bottle was sealed and stored. The stability comparison between the nitrogen foam and the methane foam at different times is shown in Figure 7.

As can be seen from Figure 7, the volume of the nitrogen foam in the sampling bottle at the initial moment is larger than that of the methane foam. This is because during the foam collection process the methane foam drains relatively quickly, and it takes a long time to fill the sampling bottle under the same conditions. With increasing time, the amount of the precipitated liquid increases for both foams, and the liquid level position remains basically constant (refer to the position of the yellow line) after 30 min. Among them, the amount of the precipitated liquid for the nitrogen foam was greater, but the volume change of the foam was smaller. After 1 h, the volume of the methane foam began to decrease significantly (refer to the position of the red line). In comparison, the volume of the nitrogen foam started to decrease after 5 h. Thus, the particle size of the foam gradually increases with time, the shape becomes increasingly irregular, and the stability of the nitrogen foam is better than that of the methane foam.

3.2. Interaction between the SiO₂ Nanoparticles and the Surfactants. To study the interaction between the SiO₂ nanoparticles and the surfactants, the dispersibility of the SiO₂ nanoparticles with different concentrations in pure water was
observed. The results are shown in Figure 8. As can be seen from Figure 8, after being left to stand for 48 h, most of the nanoparticles in the 0.5 wt % concentration dispersion were aggregated. Some of the nanoparticles in the 1.0 wt % concentration dispersion floated on the top, while some of the nanoparticles settled at the bottom. The phenomenon is similar for the 1.5 wt % dispersion and 1.0 wt % dispersion, but compared with the more suspended part, the nanoparticles in the 2.0 wt % dispersion are almost completely suspended in the upper part. Then, the viscosity of each concentration dispersion was measured and compared with the viscosity of the pure S-B solution and their mixtures. The comparison results are shown in Figure 9. Within a certain concentration range, the viscosity of the pure S-B solution is slightly greater than 1, which is close to the viscosity of water. For the pure SiO\textsubscript{2} dispersion, its viscosity gradually increases with increasing concentration, and its viscosity is the greatest at a concentration of 2.0 wt %. The burst phenomenon can be well understood in conjunction with Figure 8. For comparison, surfactant S-B at 0.1 wt % was added to each concentration of SiO\textsubscript{2} dispersion, and the viscosity did not increase suddenly at a concentration of 2.0 wt %, which indicates that the surfactants promote the dispersibility of SiO\textsubscript{2} nanoparticles in water.\textsuperscript{33}

We fixed the concentration of the SiO\textsubscript{2} nanoparticles at 1.0 wt % and added different concentrations of the S-B surfactant. Then, we studied the effect of surfactant concentration on the interfacial tension and dispersibility of the nano-SiO\textsubscript{2} dispersion. The results are shown in Figure 10. After adding the surfactant S-B, the dispersibility of the nano-SiO\textsubscript{2} dispersion liquid left standing for 48 h was improved. Relative to the dispersion, the critical micelle concentration of S-B is 0.3 wt %, which is higher than that without the addition of SiO\textsubscript{2} nanoparticles. This is because in the dispersion the SiO\textsubscript{2} nanoparticles adsorb the surfactants and enhance their dispersibility in water, and additional surfactants are required to reduce the gas–liquid interfacial tension. The final concentration of the surfactant S-B used in the nano-SiO\textsubscript{2} dispersion was 0.3 wt %.

### 3.3. Apparent Viscosity of the Foam

To conveniently compare the viscosity difference between the surfactant foam and the surfactant nanoparticle foam (denoted as surfactant-NP foam), the two foam solutions (0.1 wt % S-B solution and 0.3 wt % S-B + 1.0 wt % SiO\textsubscript{2} dispersion) were stirred and stirred.
foamed using the Waring blender method. The obtained foams were placed in the concentric cylinder sample chambers of a rheometer. The measured changes in the viscosity of the different foams over time are shown in Figure 11. The viscosities of the surfactant foam and the surfactant-NP foam initially increase and then decrease with time. This is because the foam is an unstable system that changes with time. During the foam drainage process, the quality of the foam is improved and the interaction between the bubbles is increased, which will increase the friction within the foam and increase the apparent viscosity. The viscosity of the surfactant foam reaches a maximum of 103 mPa·s after 315 s, while the viscosity of the surfactant-NP foam reaches a maximum of 156 mPa·s after 485 s. This shows that NPs can slow down foam drainage and foam deformation, thereby delaying the appearance of the foam viscosity peak. In addition, NPs adhere to the surface of the foam liquid film, increasing its structural strength and increasing the apparent viscosity of the surfactant-NP foam. As the foam coalesces and collapses, the foam liquid film becomes more fragile, and the viscosity of the foam begins to gradually decrease.\textsuperscript{34,35}\ In contrast to the surfactant foam, the surfactant-NP foam experiences a sudden drop in the viscosity during the decrease process, which is mainly because the NPs form a skeleton at the foam liquid film for protection. With the rupture of the liquid film, the skeleton is insufficient to maintain the interaction force to a certain extent, and the structure is destroyed. After that, the decrease in the viscosity of the surfactant-NP foam is similar to that of the surfactant foam. When the viscosity test time reaches 900 s, by comparing the two foams, it can be concluded that the volume of the surfactant foam decreases more than that of the original foam, and the difference in foam particle size is large. While the particle size distribution of the surface layer of the surfactant-NP foam is still uniform, the skeleton structure can be seen, and the decrease in the volume of the foam is small.

3.4. Foam Blocking Capacity. To test the blocking characteristics of the four foams, four sandpacks with almost the same porosity and permeability were created for the displacement experiments. First, water was injected with a volume of 1PV to achieve water flooding. Then, foam flooding was carried out, and the foam with a volume of 2PV was continued to be injected when the pressure began to rise steadily. Finally, subsequent water flooding was performed until the injection pressure was nearly stabilized, during which the outlet backpressure was maintained at 1.2 MPa. The change in the injection pressure curve during the injection process is shown in Figure 12. In the water flooding stage, the injection pressures of the four groups of curves remained stable at about 1.2 MPa, and the foam flooding stage was the stage with the largest difference. After the injection of the N\textsubscript{2} foam with 1PV (corresponding to the abscissa at 2PV), the injection pressure started to increase, and after the injection with 2PV (corresponding to the abscissa at 4PV), the pressure reached a maximum of 2.3 MPa. After the injection of the CH\textsubscript{4} foam with 2.6PV (corresponding to the abscissa at 3.6PV), the injection pressure began to increase, and after the injection with 2PV (corresponding to the abscissa at 5.6PV), the pressure reached a maximum of 2.0 MPa. In the subsequent water flooding phase, both the N\textsubscript{2} foam curve and the CH\textsubscript{4} foam curve decreased rapidly until they stabilized. However, the injection pressure of the N\textsubscript{2}/NP foam started to increase after the injection volume of 0.4PV (corresponding to the abscissa at 1.4PV). After the injection of the 2PV foam continued (corresponding to the abscissa at 3.4PV), the pressure continued to increase. Until the subsequent water flooding with 0.1PV (corresponding to the abscissa at 3.5PV), the pressure reached a maximum of 3.9 MPa. After the CH\textsubscript{4}/NP foam with 2.1PV (corresponding to the abscissa at 3.1PV) was injected, the injection pressure started to increase. After the injection with 2PV (corresponding to the abscissa at 5.1PV) continued, the pressure increased until the subsequent water flooding with 0.1PV (corresponding to the abscissa at 5.2PV) and the pressure reached a maximum of 3.2 MPa. In comparison, during the foam flooding stage, foams with NPs added under the same gas conditions have faster pressure increases than foams without NPs. At the end of the foam flooding stage, the foaming pressure without adding NPs reached the maximum, while the foaming pressure with NPs added had not yet ended, and the injection pressure reached the maximum after a period of subsequent water flooding. To some extent, this indicates that the addition of nanoparticles...
can promote the stability of the foam, and in the subsequent water flooding process, several weak plugs can be formed, and then, the injection pressure starts to decrease. Regardless of whether NPs are added or not, the pressure increase rate and the amplitude of the methane foam are weaker than those of the nitrogen foam, which is related to the properties of methane and nitrogen. 29

We placed the foam generated before blocking on a glass slide, covered with a cover glass, and observed the change in its shape with time under a microscope. We used three time nodes (initial time, 5 min, and 10 min) to compare the particle size changes and particle size normal distribution curves of the four foams, as shown in Figure 13. The steeper the normal distribution curve, the more uniform the foam particle size distribution. The abscissa corresponding to the peak of the curve is approximately the average particle size. The foam distribution curve, the more uniform the foam particle size distribution. The abscissa corresponding to the peak of the curve is approximately the average particle size. The foam equivalent diameter distributions at the initial time and at the final time (10 min) were compared, as shown in Figure 14.

![Figure 13. Micromorphological changes in the foam. (a) N₂ foam, (b) N₂/NP foam, (c) CH₄ foam, and (d) CH₄/NP foam at 25 °C.](image)

By combining Figures 13 and 14, we found that as far as reinforced foams with nanoparticles and ordinary foams without nanoparticles are concerned, at the initial moment, the overall equivalent diameter of the surfactant-NP foam is small and the amount of foam is large. This can also be seen from the larger frequency value of the equivalent diameter of the NP foam at the initial moment of the foam, as shown in Figure 14. It can be seen that when the equivalent diameter is 50 μm, the cumulative frequency of the surfactant-NP foam is about 0.4, while the cumulative frequency of the surfactant foam is less than 0.1. At 5 min, the difference between the two foams is not large, but at 10 min, it is obvious that the equivalent diameter of the surfactant foam becomes larger and the shape becomes irregular. The equivalent diameter distribution of the surfactant-NP foam is relatively uniform. As can be seen from Figure 14, the slope of the cumulative frequency of the surfactant-NP foam becomes large. When the equivalent diameter is about 700 μm, the cumulative frequency of the NP foam is 1, and after the equivalent diameter exceeds 1000 μm, the cumulative frequency of the ordinary foam has not yet reached 1. This is because the NPs prevent the foam liquid membrane from draining, thereby slowing down the coalescence and disproportionation of the foam. As far as the nitrogen foam and methane foam are concerned, the cumulative frequency curve of the nitrogen foam rises faster and the corresponding value is larger for the general trend, which indicates that the nitrogen foam is more stable. Compared with the nitrogen foam, the methane foam has a faster drainage rate, and the diameter of the foam at the final moment is slightly larger, which also verifies the properties of the methane gas mentioned earlier.

3.5. Foam Flooding Characteristics. We tested the oil displacement ability of nitrogen and methane foams in the presence or absence of nanoparticles using a microscopic model. It was found that under the same conditions, the oil displacement effects of the nitrogen foam and methane foam are close, which is related to the experimental conditions of the microscopic model. Here, only the oil displacement effect of the methane foam in the presence or absence of nanoparticles is compared, as shown in Figure 15. This can also be used as a comparative reference for the oil displacement effect of the nitrogen foam in the presence or absence of nanoparticles. In order to make the results more intuitive, the flooding fluid was dyed, the water was dyed red, and the foam was dyed blue.

As shown in Figure 15a,d, after water flooding, crude oil was used from the dominant part of the entrance to the exit in the microscopic model, and there was a large amount of residual oil in the unfluidized area of the injection fluid in the upper and lower parts of the model. Due to the difference in mobilities of water and oil, the locations the water can reach are limited. After switching the displacement fluid, the degree of utilization of the remaining oil improved, as can be seen in Figure 15b,e. By comparing the surfactant foam flooding with the surfactant-NP foam flooding, we found that the surfactant-NP foam flooding has a larger sweep volume. In the microscopic model, a great deal of blind residual oil was effectively utilized because the surfactant-NP foam has a higher apparent viscosity compared with the surfactant foam, thus improving the mobility ratio. However, since it also has a stronger plugging performance, it can adjust the flow of the dominant channel. Near the middle of the line connecting the inlet and the outlet, both surfactant foam flooding and surfactant-NP foam flooding fully utilize the crude oil there.
We selected this position to zoom-in on, as shown in Figure 15c,f. After adding NPs, the oil washing efficiency of the foam was significantly improved. This is because the NPs can be irreversibly adsorbed onto the liquid film of the bubble interface, and a dense layer is formed at the interface through flocculation, which increases the viscoelasticity of the surfactant-NP foam’s liquid film.36

By analyzing and calculating the distribution of crude oil in the microscopic model, the recovery factor of crude oil after water flooding and after methane foam flooding is shown in Figure 16. Under the same conditions in the two groups of experiments, the crude oil recovery factor after water flooding was basically the same, and the difference in the crude oil recovery factor after foam flooding was obvious. After surfactant foam flooding, the final crude oil recovery factor was 55.85%, which was increased by 41.5% from 47.25% after water flooding. Thus, the residual oil after water flooding can be effectively utilized by foam flooding. The surfactant-NP foam flooding has a better oil displacement effect and can enhance the recovery factor by more than 30%.

The above foam flooding tests in the presence or absence of nanoparticles were performed in parallel groups. To compare the two types of foam flooding effects more directly, the same set of flooding experiments were performed in the microscopic model. The distribution of the remaining oil after replacement is shown in Figure 17. At the same model position, a large amount of residual oil still adheres to the wall surface after water flooding, and the dead oil at the dead end (marked by the red dotted line) has not been used. The surfactant foam flooding utilizes some of the remaining oil and changes the oil-water distribution. However, the surfactant foam is easily deformed and has relatively poor stability, resulting in dead-end dead oil that has not been effectively used. The surfactant-NP foam has a dense and uniform distribution and a strong liquid film, and it is difficult to change its shape. Therefore, after the displacement of the surfactant-NP foam, the remaining oil in this part is almost completely utilized, and the volume of the dead-end dead oil has been compressed by more than 1/3 by the surfactant-NP foam. Thus, the surfactant-NP foam has a significant oil displacement effect.

Based on the above analysis, a schematic diagram of the surfactant-NP foam’s mobile residual oil process was created and is shown in Figure 18. It is summarized from actual experimental phenomena (Figure 18c,d) and compared with the surfactant foam. Surfactant molecules have a hydrophilic end and a hydrophobic end. On the foam liquid membrane, the hydrophobic end is distributed within the gas phase and the hydrophilic end is dispersed in the liquid phase. The increase in the concentration of surfactant molecules may cause the hydrophilic end of the surfactant molecule, which is free in the liquid phase, to bind to the hydrophilic end of the surfactant molecule on the surface of the liquid film. The hydrophobic end of the agent molecule achieves certain

Figure 15. Comparison of the oil recovery effects of surfactant foam flooding and surfactant-NP foam flooding in the microscopic model: (a) after water flooding, (b, c) after surfactant foam flooding, (d) after water flooding, and (e, f) after surfactant-NP foam flooding.

Figure 16. Comparison of oil recovery factor after water flooding and after methane foam flooding.

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adsorption when it comes in contact with the oil droplets, as shown in Figure 18a. However, the number of surfactant molecules capable of forming adsorption is few, and the adsorption force formed is extremely limited, which is why the oil washing efficiency of surfactant foam is poor. The hydrophobic NPs can be irreversibly adsorbed on the liquid film of the bubble interface, and a dense layer is formed on the interface through flocculation. In addition, there may be NPs that are free in the liquid phase, and the surface adsorbs surfactant molecules to ensure the dispersion in the liquid phase. This part of the original free NPs reassociates with the surfactant molecules on the foam’s liquid membrane through the hydrophilic end of the self-bound surfactant molecules. This results in the NPs being exposed on the outside of the foam’s liquid film, and the hydrophobic ends of some of the surfactant molecules can be well adsorbed on the oil droplets and generate a large viscous force, which is beneficial to the fall off of the oil droplets, as shown in Figure 18c. In addition, Sun et al. confirmed that the viscoelasticity of the surfactant-NP foam’s liquid film is improved compared to that of the surfactant foam’s liquid film. In the oil displacement process, it is more difficult to change the shape of the foam. The surfactant-NP foam can generate more force in the displacement direction, which can displace more crude oil.

It should be noted that although the displacement effects of the nitrogen foam and methane foam are similar in the microscopic model, we suspect that there will be a difference in the displacement of the two foams under actual reservoir conditions. Both types of foams can adjust the displacement profile to a certain extent during the displacement process. The state at this time is called foamed gas. Although the stability of the methane foam is not as good as that of the nitrogen foam, it can reach the free gas state after the foam bursts. It has been demonstrated that the solubility of methane in crude oil is much greater than the solubility of nitrogen in crude oil, which means that after the methane bubble bursts, part of the methane is inefficiently displaced and part of the methane is trapped in the formation. However, part of the methane gas easily dissolves in the crude oil under high pressures, forming foam oil, which causes the density and viscosity of the crude oil to decrease. This facilitates the flow of crude oil during the displacement process, resulting in higher oil recovery.
4. CONCLUSIONS

The properties and applications of the methane foam were evaluated and compared with those of the widely used nitrogen foam, and the performance changes of the two types of foams after adding nanoparticles were compared. The following four major conclusions were drawn from the results of this study:

(1) Methane and nitrogen foams produced using the jet method for three types of compound surfactants were compared. An anionic–amphoteric surfactant was determined to be superior. The initial foam volume of the methane foam was larger than that of the nitrogen foam, but its static stability was poor. The half-life of the methane foam was about half that of the nitrogen foam.

(2) Through interfacial tension and viscoelastic modulus tests, the optimum CMC was reached when the S-B surfactant concentration was 0.1 wt %. After adding 1.0 wt % SiO2 nanoparticles, the surfactant concentration needed to be 0.3 wt % to reach the CMC. The viscosity of the dispersion increased slightly. As for the maximum foam viscosity, that of the surfactant-NP foam increased by 53 mPa·s compared with that of the surfactant foam, and the stability was enhanced.

(3) Nitrogen foam and methane foam sandpack plugging experiments were performed with and without nanoparticles. The plugging performance of the methane foam was lower than that of the nitrogen foam. After adding SiO2 nanoparticles, the plugging performances of both foams improved. By observing the change in morphologies of the foams, it was found that the drainage and aggregation of the methane foam were faster than those of the nitrogen foam. After adding SiO2 nanoparticles, the uniformity of the diameter of the foam improved.

(4) Oil displacement experiments were performed on the nitrogen foam and methane foam with and without nanoparticles. The oil displacement effects of the methane and nitrogen foams were similar. After adding SiO2 nanoparticles, the swept volume and oil washing efficiency of the foams improved. The surfactant-NP foam flooding has a better oil displacement effect and can enhance the recovery factor by more than 30%. After the foam burst, the solubility of methane in crude oil was better than that of nitrogen. The application of methane foam in actual oilfields needs further verification.

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Notes
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