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Polyethylene Glycol Drilling Fluid for Drilling in Marine Gas Hydrates-Bearing Sediments: An Experimental Study

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Abstract: Shale inhibition, low-temperature performance, the ability to prevent calcium and magnesium-ion pollution, and hydrate inhibition of polyethylene glycol drilling fluid were each tested with conventional drilling-fluid test equipment and an experimental gas-hydrate integrated simulation system developed by our laboratory. The results of these tests show that drilling fluid with a formulation of artificial seawater, 3% bentonite, 0.3% Na₂CO₃, 10% polyethylene glycol, 20% NaCl, 4% SMP-2, 1% LV-PAC, 0.5% NaOH and 1% PVP K-90 performs well in shale swelling and gas hydrate inhibition. It also shows satisfactory rheological properties and lubrication at temperature ranges from −8 °C to 15 °C. The PVP K-90, a kinetic hydrate inhibitor, can effectively inhibit gas hydrate aggregations at a dose of 1 wt%. This finding demonstrates that a drilling fluid with a high addition of NaCl and a low addition of PVP K-90 is suitable for drilling in natural marine gas-hydrate-bearing sediments.

Keywords: marine gas hydrate; drilling fluid; polyethylene glycol; kinetic inhibitor

1. Introduction

Gas hydrates are clathrate non-stoichiometric compounds, in which the molecules of gas are engaged in crystalline cells, consisting of water molecules retained by the energy of hydrogen bonds [1]. They are also called clathrate hydrates or “flammable ice” [2]. Natural-gas hydrates are distributed widely in marine continental margin sediments and permafrost environments, with the overwhelming majority of hydrate reservoirs discovered existing in the former location [3]. It is believed that the energy in these hydrate deposits is likely to be significant compared to other types of fossil fuel deposits [4,5]. Since natural gas hydrates have the attributes of high energy density, large reserves, and relative cleanliness [6], they are currently considered a potential unconventional energy resource [7,8].

During the process of exploring and exploiting this energy resource, drilling is the most direct and important approach. When drilling in oceanic gas-hydrate-bearing sediments, the disturbance of *in situ* formations by drilling can alter the conditions and make gas hydrates unstable. The dissociation of gas hydrate can lead to a series of problems related to drilling safety. In the case of an uncased borehole, the gas-hydrate dissociation will cause the borehole to become unstable, and the gas released by gas-hydrate dissociation will erode the drilling pipe and leak at the seafloor [9–13]. The gas circulated with drilling fluids may also re-form as a hydrate, blocking the drilling pipe terminating the fluid circulation [14–16]. In addition, the abundance of gas may result in blowouts at the surface or gasifying the seawater, which would cause the platform to lose buoyancy and possibly collapse. If the borehole is cased, the high pressure accompanied by gas-hydrate dissociation may cause casing failure and borehole collapse. In recent decades, the petroleum industry has expanded drilling operations into deep-water areas, and the pace of gas-hydrate exploitation has accelerated. Because of this, the problems related to conventional oil or gas drilling in deep water or marine hydrate reservoirs must be taken into consideration. Barker *et al.* [14] first reported two drilling accidents involving gas hydrate formation in drilling fluids, one at Santa Barbara, California, and the other at Green Canyon in the Gulf of Mexico. Birchwood *et al.* [17] concluded that by cooling drilling fluid and decreasing the circulation rate, the influence of drilling through gas-hydrate-bearing sediments on petroleum operations can be minimized. Therefore, it is important to take appropriate efforts to minimize gas-hydrate dissociation or inhibit the formation of gas hydrate within the drill string or annulus to ensure safe drilling operations. This matter depends on the rational drilling fluids system. The choice of drilling fluids plays an important role in achieving the above-mentioned objectives.

In order to overcome the problems that might be encountered during drilling in oceanic gas-hydrate-bearing sediments, a suitable drilling-fluid system should have the following characteristics:

- (1) The relative density (ρ) of the drilling fluid must have an appropriate changing range. The drilling fluid can supply a definite pressure to counteract the stratum and prevent hydrates around the borehole from decomposing to keep the borehole wall stable. For a practical situation of hydrates sediment, results of previous experiments in our lab indicate the optimum relative density is in the range of 1.05–1.2 [18], according to the safe density window of drilling fluid.
- (2) The drilling fluid should be able to effectively inhibit shale hydration and gas-hydrate aggregations in the drilling pipe and blowout preventer.

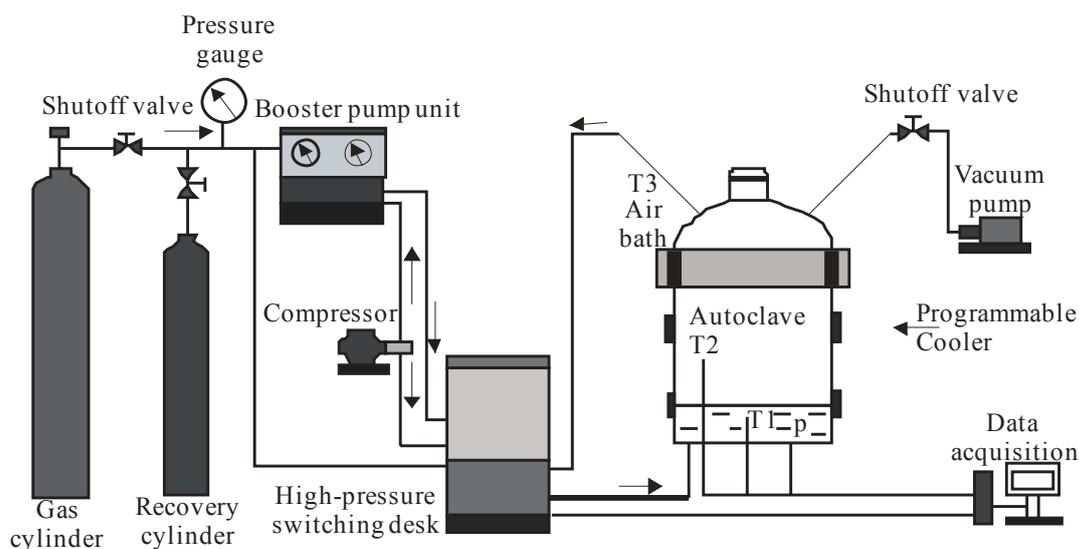
- (3) The drilling fluid should have a low temperature that can effectively prevent the dissociation of hydrates around the borehole.
- (4) The drilling fluid should have good rheological properties and stability at low temperatures.
- (5) The drilling fluid should prevent calcium- and magnesium-ion pollution. Normally, the concentration of calcium and magnesium ions in the ocean is about 0.40 g/kg and 1.28 g/kg, respectively [19]. Though these percentages are very small, they can greatly influence the performance of the drilling fluid.
- (6) The drilling fluid must have sufficient lubrication and low filtration.

At present, the typical drilling-fluid system used in offshore drilling is a polymer drilling fluid containing salts and organic agents, which are well-known thermodynamic hydrate inhibitors. Water-based polymer drilling fluids with a high salt content and partially hydrolyzed polyacrylamide (PHPA) have been successfully used in many deep-water drilling activities [20,21]. In most cases, the thermodynamic inhibitors are added into drilling fluids to prevent gas-hydrate formation in deep water drilling, whereas the results of kinetic hydrate inhibitors (KHIs) are still under investigation [22–24]. Compared with traditional thermodynamic inhibitors, kinetic inhibitors are effective at very low addition (generally 0.01–1 wt%), which can significantly reduce the drilling cost. At the same time, kinetic inhibitors are more environmentally friendly and could be applied under more and more restrictive regulations [25]. In addition, for deep-water drilling in gas-hydrate-bearing sediments, the use of thermodynamic inhibitors for hydrate inhibition should be considered carefully because they prevent hydrate aggregations in the borehole, but can also cause the dissociation of hydrates occurring around the borehole sediment if their concentration is too high [26], which can then affect borehole stability. Because of this, KHIs or anti-agglomerants (AAs) should also be considered for preventing hydrate aggregations that may form during marine gas-hydrate drilling. In this work, we develop a formulation of polyethylene-glycol drilling fluid with added KHI specially designed for drilling in gas-hydrate-bearing sediments. We simulate the conditions encountered in deep-water drilling and evaluate the performance of the drilling fluid. The shale inhibition, low-temperature performance, ability to prevent calcium- and magnesium-ion pollution, and hydrate inhibition of the polyethylene glycol drilling fluid were each tested by employing conventional drilling-fluid test equipment and a gas-hydrates integrated-simulation experimental system developed by our laboratory.

2. Experimental

2.1. Apparatus

The conventional performance test equipment used for testing the drilling fluid includes a mud densimeter, a ZNN-D6 rotational viscosimeter, an HAPI filter press and a ZNP swelling amount tester. The experimental gas-hydrate integrated simulation system was used to test the inhibition of hydrate formation in drilling fluid. This system has also been used in our previous work [27]. It was developed to run various hydrate and drilling-fluid simulation tests. A schematic of the experimental apparatus is shown in Figure 1.

Figure 1. Schematic diagram of the experimental gas-hydrate integrated simulation system.

2.2. Materials

The polyethylene glycol used in the experiments was produced by Shanghai Shiyi Chemical Reagent Co. Ltd. Its average relative molecular weight is 2000 ± 10 . The kinetic inhibitor polyethylene pyrrolidone PVP K-90 was made by Henan BoAi Pharmaceuticals Co. Ltd. The methane was provided by Wuhan Huaxing Industrial Technology Co. Ltd., with a purity of 99.9%. The other reagents used in this drilling fluid were commonly used products produced by well-known companies.

2.3. Principles and Procedure

Due to the fact that seawater has been used as the drilling fluid for most offshore drillings, we used it to make the drilling fluid. For our experiment, man-made seawater was employed. The salinity of our man-made seawater was about 3.4%, which is common for natural seawater worldwide. According to the laboratory research and practical drilling operations, drilling fluid containing 10% polyethylene glycol and 20% NaCl has a relatively comprehensive performance [28,29], so the designed formula for our polyethylene-glycol drilling fluid for marine gas-hydrates drilling is artificial seawater, 3% sodium bentonite, 1% LV-PAC, 4% SMP-2, 10% polyethylene glycol, 20% NaCl, 1% PVP K-90 and 0.5% NaOH. The formula and the concrete concentration of each component were designed based on our and other researchers' previous work [30–32]. All the percentages are expressed in mass ratios. In this formula, low-viscosity polyanionic cellulose (LV-PAC) and sulfomethylated phenolic resin (SMP-2) can reduce the filtration of drilling fluid, and PVP K-90 is a kinetic hydrate inhibitor. Since 1990s, many types of KHIs have been developed [25]. The PVP was considered the first generation of KHIs. Although the subsequent KHIs such as PVCap and Gaffix VC-713 outperform PVP, the PVP is the basic one and has relatively easier acquisition and lower cost compared with these KHIs. So it is selected as the hydrate inhibitor in our study. In addition, the addition of NaOH can adjust the pH value of the drilling fluid.

The normal performance of the polyethylene-glycol drilling fluid was tested using the conventional equipment. The ZNP swelling amount tester was used to test the shale inhibition. The mud densimeter,

the ZNN-D6 rotational viscosimeter and the HAPI filter press were used to test the density, rheology and filtration at low temperatures, respectively. In the low-temperature tests, the drilling fluid and the test equipment were put into a programmable cooler according to the order of corresponding tests. The programmable cooler was set at a predefined temperature to cool the drilling fluid. When the cooler reached the predefined temperature, the drilling fluid was stirred every ten minutes for one hour, allowing the drilling fluid to reach a uniform temperature. Then, the corresponding tests were performed. Next, the hydrate inhibition of the drilling fluid was tested by the simulation experimental system shown in Figure 1. About 2000 mL of drilling fluid and some methane were injected into an autoclave until the pressure in the autoclave reached 18 MPa. The autoclave was kept in the programmable cooler which was set at 4 °C for 20 hours. This temperature (4 °C) and pressure (18 MPa) simulate the conditions in water at a depth of 1800 m. Because the formation of hydrate consumes gas and releases heat, the pressure inside the autoclave would decrease and its temperature would increase during the experiments. These changes could then be used to evaluate hydrate formation in the drilling fluid and the effectiveness of the inhibitor used.

3. Results and Analysis

3.1. Shale Inhibition

There are two common methods for shale-inhibition evaluation: The dispersing inhibition test (rolling collection test) and the expansion inhibition test. Here, the shale expansion tests were conducted and compared with a pure-water system. The results are shown in Table 1.

Table 1. The results of the shale expansion experiments.

| Test System | Linear Expansivity (%) | | | | | | | |
|---------------------------|------------------------|------|------|------|------|------|------|------|
| | 2 h | 4 h | 6 h | 8 h | 10 h | 12 h | 14 h | 16 h |
| Pure water | 6.8 | 14.3 | 27.7 | 33.5 | 36.7 | 39.0 | 39.8 | 40.5 |
| The drilling fluid system | 3.2 | 6.8 | 8.5 | 9.7 | 11.5 | 12.9 | 13.5 | 13.8 |

As can be seen in Table 1, the polyethylene-glycol drilling fluid has a significant inhibition on shale expansion. After two hours, the linear expansivity of shale in drilling fluid was only 3.2%, a reduction of 52.94% compared to that in pure water. After 16 h, the linear expansivity of shale in drilling fluid was 13.8%, a reduction of 65.93% compared to that in pure water. Furthermore, as can be seen from Figure 2, the linear expansivity of shale in pure water had a significant growth trend throughout the whole test, while the linear expansivity of shale in the polyethylene-glycol drilling fluid was changed very slowly.

3.2. Properties at Low Temperature

The temperature of circulating drilling fluid is normally about 0 °C to 6 °C when drilling in deep water. For our test, we expanded the possible range of circulating drilling fluid temperatures to range from −8 °C to 15 °C. The density (ρ), rheology (plastic viscosity (PV), gel strength (Gel), and yield point (YP)) and filtration (FL) of the drilling fluid were each tested.

Figure 2. The shale expansion in the pure water and the drilling fluid.

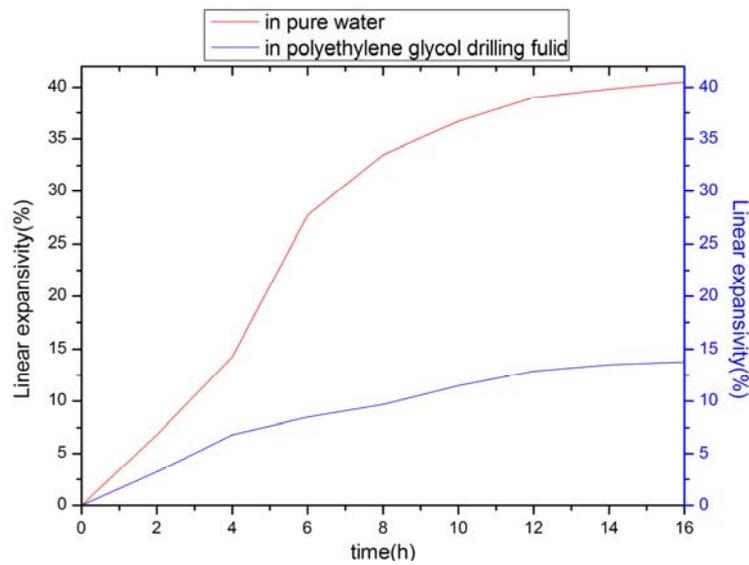
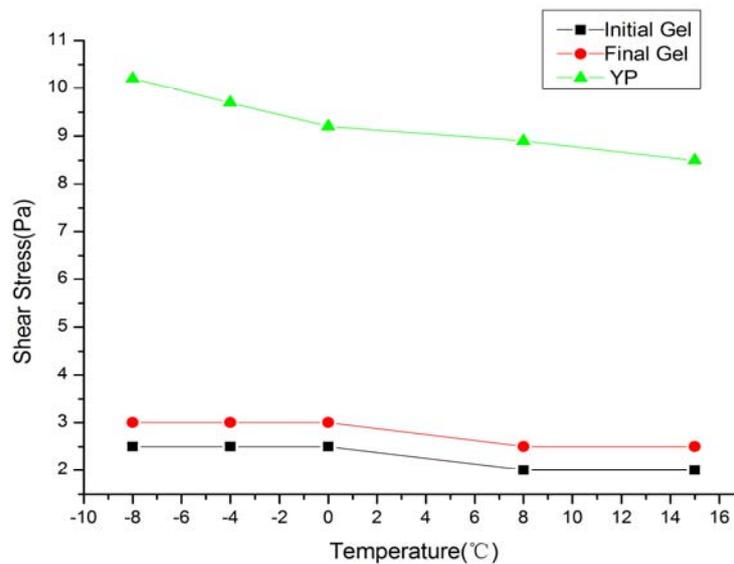


Table 2. The rheological properties of polyethylene-glycol drilling fluid at different temperatures.

| T (°C) | ρ (g/cm ³) | <i>Gel</i> (Pa/Pa) | <i>PV</i> (mPa·s) | <i>YP</i> (Pa) | <i>FL</i> (mL) |
|----------|-----------------------------|--------------------|-------------------|----------------|----------------|
| 15 | 1.15 | 2/2.5 | 18 | 8.5 | 5.5 |
| 8 | 1.15 | 2/2.5 | 20 | 8.9 | 5.5 |
| 0 | 1.16 | 2.5/3 | 21 | 9.2 | 5.5 |
| -4 | 1.16 | 2.5/3 | 22 | 9.7 | 5.7 |
| -8 | 1.16 | 2.5/3 | 25 | 10.2 | 5.8 |

Figure 3. The change of gel strength and yield point of polyethylene glycol drilling fluid at different temperatures.



These results are shown in Table 2. As can be seen from Table 2 and Figure 3, the *PV* and *Gel* value had increasing trends, but the changes were small and acceptable. Furthermore, the high ratios of yield point and plastic viscosity would help to carry cuttings and clean the borehole. Although filtration had

an increasing trend, it showed very little change. In conclusion, the polyethylene glycol exhibited good performance as measured by rheological properties and stability at low temperature.

3.3. Prevention of the Pollution Caused by Calcium and Magnesium Ions

During the drilling operation process, sediment water and seawater containing calcium and magnesium ions can enter into the borehole and mix with drilling fluids, which pollutes the drilling fluids and changes their performance. To test the ability of the drilling fluid to prevent pollution from calcium and magnesium ions, experiments were performed by adding different amounts of $MgCl_2$ and $CaCl_2$ into the polyethylene-glycol drilling fluid in the laboratory. The test results are shown in Table 3. The shear viscosity of drilling fluid increased with increased amounts of $MgCl_2$ and $CaCl_2$, but the change was very small, as was the filtration. In other words, the polyethylene-glycol drilling fluid has an excellent anti-pollution ability against calcium and magnesium ions.

Table 3. Experiment for preventing pollution by calcium and magnesium ions.

| Formula | PV (mPa.s) | YP (Pa) | Gel (Pa/Pa) | FL (mL) |
|---|------------|---------|-------------|---------|
| The drilling fluid | 18.0 | 8.5 | 2/2.5 | 5.5 |
| The drilling fluid + 0.3% $MgCl_2$ + 0.1% $CaCl_2$ | 18.5 | 9.2 | 2.5/3 | 5.5 |
| The drilling fluid + 0.51% $MgCl_2$ + 0.18% $CaCl_2$ | 20.0 | 9.0 | 3/3.5 | 5.8 |
| The drilling fluid + 0.8% $MgCl_2$ + 0.4% $CaCl_2$ | 21.5 | 9.0 | 3/3.5 | 5.8 |

3.4. Hydrate Inhibition

To test hydrate inhibition, the drilling fluid without PVP K-90 was injected into the autoclave and cooled to 4 °C by the programmable cooler under 18 MPa pressure. The whole cooling time was 20 h. During the experiment, the pressure and the temperature in the autoclave changed significantly (Figure 4a). The pressure decrease significantly from 18 MPa at the beginning to 13.5 MPa at the end. At the beginning of experiment, the pressure reduced slowly because some methane gas was dissolving in the drilling fluid. The temperature had a sharp rise when the experiment lasted for 900 min, which could indicate that there were a large number of hydrates formed. This also implies that only relying on the thermodynamic inhibitors (in this case, the drilling fluid contains 20% NaCl) can not fully prevent hydrate formation and aggregation under this temperature and pressure. Under the same conditions, drilling fluid with 1 wt% PVP K-90 was injected into the autoclave. The results showed no significant change in temperature and pressure in the autoclave over 20 hours (Figure 4b). The pressure was 18 MPa at the beginning and 17.5 MPa at the end, and the lost 0.5 MPa was likely due to the methane dissolution in the drilling fluid (the solubility of methane at 18 MPa, 4 °C in the 20% NaCl solution is about 34.32 mM [33], the corresponding dissolution gas volume in the drilling fluid is about 1.5 L at standard condition). Furthermore, the temperature in the autoclave showed almost no change. This indicates that no hydrates formed in the autoclave. This experiment shows that a low dose of PVP K-90 has excellent performance on hydrate-formation inhibition, and the polyethylene-glycol drilling fluid is able to effectively inhibit gas-hydrate formation at low

temperature and high pressure. The inhibition would be even more obvious with the addition of more PVP K-90. However, since it is a macromolecule polymer, adding too much PVP K-90 would inevitably lead to excessive shear viscosity. Table 4 shows the effect of PVP K-90 on the rheological properties of polyethylene-glycol drilling fluid. It can be found that the gel strength and yield point of drilling fluid are preferable when the concentration of PVP K-90 increases to 1%, especially the plastic viscosity that reaches 20 mPa·s.

Figure 4. The contrast of temperature and pressure evolution of polyethylene glycol drilling fluid with and without the addition of PVP K-90 (a) in absence of PVP and (b) in presence of PVP.

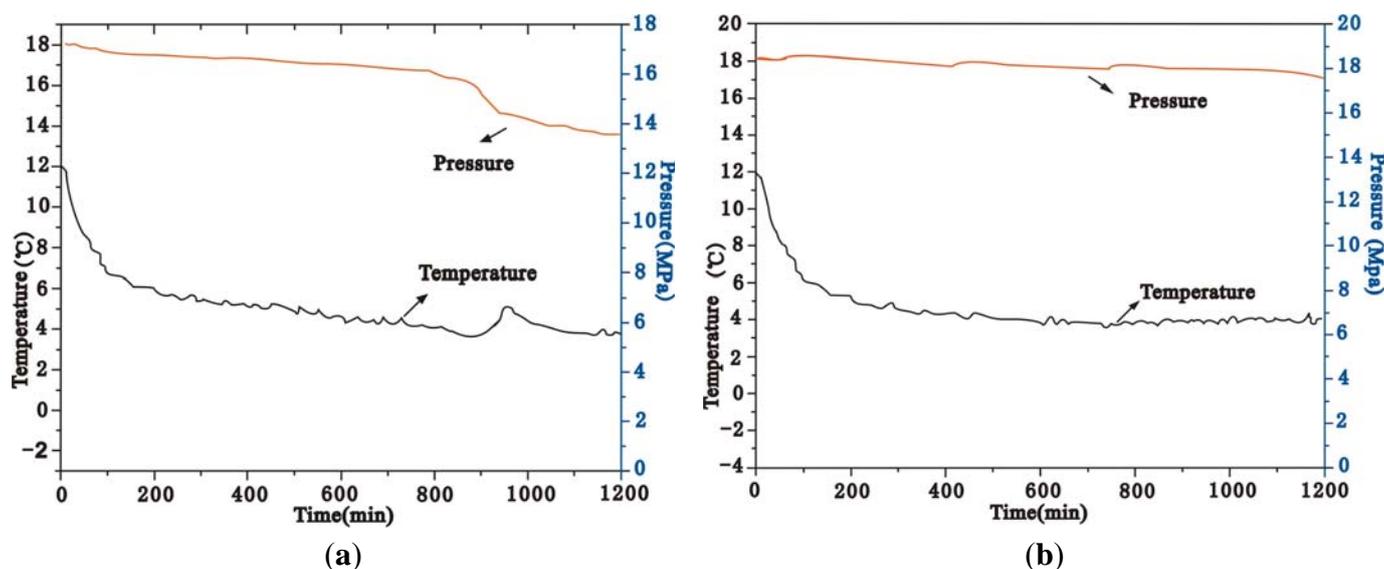


Table 4. The rheological properties of polyethylene-glycol drilling fluid with different PVP K-90 concentration.

| PVP Content | ρ (g/cm ³) | Gel (Pa/Pa) | PV (mPa.s) | YP (Pa) | FL (mL) |
|-------------|-----------------------------|-------------|------------|---------|---------|
| 0.4% | 1.165 | 1.5/2.0 | 12.0 | 5.1 | 11.0 |
| 0.5% | 1.165 | 1.5/2.0 | 13.0 | 5.1 | 10.8 |
| 0.6% | 1.165 | 1.0/2.0 | 14.5 | 6.6 | 10.4 |
| 0.7% | 1.166 | 1.5/2.5 | 16.8 | 3.6 | 9.5 |
| 0.8% | 1.166 | 1.5/2.0 | 18.0 | 4.6 | 7.8 |
| 0.9% | 1.167 | 2.0/2.5 | 18.5 | 8.7 | 6.5 |
| 1.0% | 1.168 | 2.0/2.5 | 20.0 | 9.2 | 5.5 |
| 1.1% | 1.168 | 2.0/3.0 | 22.5 | 8.7 | 5.5 |
| 1.2% | 1.168 | 2.5/4.5 | 23.0 | 9.7 | 5.5 |

Besides, the yield point/plastic viscosity ratio approaches 0.46, which also shows that the drilling fluid has good rheological properties and can effectively lubricate drilling tools, suspend drilling cuttings and stabilize boreholes. If the concentration of PVP K-90 increases more than 1%, the rheological properties of drill fluid become worse, which will influence the circulation rate of drilling fluid and even cause pressure surges in the borehole. Therefore, the concentration of 1% PVP K-90

can achieve the balance of good hydrate inhibition and relatively suitable rheology behavior in the polyethylene-glycol drilling fluid over at least 20 h at 18 MPa pressure and low temperature.

4. Conclusions and Suggestions

(1) The designed polyethylene-glycol drilling-fluid system has good performance concerning shale and gas-hydrate inhibition, rheological properties and stability at low temperature. Its density is also appropriate for this application. This drilling fluid can effectively prevent pollution caused by calcium and magnesium ions. Therefore, it is able to maintain borehole stability, suspend drilling cuttings, and clean the bottom of the borehole while drilling.

(2) If sea depth exceeds a certain value, only relying on the thermodynamic inhibitors (in this case, the drilling fluid contains 20% NaCl and 10% polyethylene glycol) can't fully prevent hydrate formation in the designed drilling fluid. Adding a small amount of the kinetic inhibitor PVP K-90 into the polyethylene-glycol drilling fluid can effectively inhibit hydrate nucleation and aggregation; it can also prevent the gas dissociated from hydrates around the borehole from re-forming as hydrates later in the cycle pipeline.

(3) While drilling in gas-hydrate-bearing formations, it is suggested that the drilling fluid have a high circulating speed to inhibit gas-hydrate decomposition and reformation. Because the heat produced by auger cutting stratum can be rapidly dissipated by the drilling fluid, the drilling fluid can be renovated rapidly. This process is helpful for cooling the drilling fluid by the cold water around drill pipes in deep seas, which can help control dissociation of the hydrates around the borehole and wellbore stability.

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