Environmental-friendly drilling fluid system in offshore natural gas hydrate formations

Yubin Zhang¹, Zhengsong Qiu¹*, Xin Zhao¹, Yongle Ma², Jiaxing Mu¹, Yunfan Liu¹
¹School of Petroleum Engineering, China University of Petroleum, Qingdao, China
²Boxing Division of CNPC Offshore Engineering Company Limited, Tianjin, China
*Corresponding author (Zhengsong Qiu).
E-mail: B18020010@s.upc.edu.cn

Abstract. There are abundant natural gas hydrate resources in offshore. However, the development of drilling fluid system is restricted by low ambient temperature, special formation conditions of weak cementation and high environmental protection requirements of marine discharge. In this paper, a new environmental-friendly drilling fluid system in offshore gas hydrate formations has been developed by optimizing the additives. The comprehensive evaluation shows that the freezing point of the drilling fluid can reach -10 °C, and it still has good rheological properties at 4 °C. The apparent viscosity ratio of the drilling fluid is less than 1.3, and the fluid filtration is only 4 mL. With good shale hydration inhibition, it can significantly reduce the swelling ratio and increase the cutting dispersion recovery ratio. There is no hydrate formation in drilling fluid for 24 hours at 4 °C and 10 MPa simulated conditions, which shows a good ability to inhibit gas hydrate formation. At the same time, compared with the experimental fluid without hydrate decomposition inhibitor, the drilling fluid can delay hydrate decomposition. In addition, the drilling fluid has good environmental protection performance, which can meet the requirements of high environmental protection in offshore.

1. Introduction
Natural gas hydrate has wide distribution, large resources and little pollution, which is considered as a new clean energy to replace traditional fossil energy in the future [1-3]. The proven natural gas hydrate reserves in the world are about $21 \times 10^{15}$ m³, and its carbon content is about twice that of fossil fuels (total oil, natural gas and coal) [4-6]. When drilling in offshore natural gas hydrate formations, it is necessary to consider that drilling fluid intrudes into hydrate formation, which leads to hydrate decomposition, resulting in wellbore instability, poor rheological properties of drilling fluid, lower formation strength and other problems [7-10]. Moreover, the gas produced by decomposition may generate natural gas hydrate again at low temperature and plug the wellbore [11-15].

Therefore, by adding 10% sodium chloride (NaCl) to adjust the freezing point of the drilling fluid, compounding xanthan gum (XC) and a new salt resistant agent SCH, an environmental-friendly low-temperature water-based drilling fluid formula has been developed, and its rheological property, filtration property, shale hydration inhibition, hydrate formation inhibition and environmental performance were evaluated. A set of environmental-friendly low-temperature water-based drilling fluid system for hydrate formation in offshore was constructed. And it is expected to provide
environmental-friendly drilling fluid technical support for the independent exploration and development of natural gas hydrate resources in offshore.

2. Experimental

2.1. Materials
In this experiment, high quality sodium bentonite was selected. NaCl was used to reduce the freezing point of drilling fluid and effectively inhibit the formation of hydrate in wellbore. The new viscosity increasing and filtration reducing agent SCH combined with XC had good salt resistance and low viscosity temperature coefficient. Carboxymethyl starch (CMS) was used as filtrate reducer and ultrafine calcium carbonate (CC) as plugging agent. Polyvinylpyrrolidone (PVP) was used as hydrate decomposition inhibitor, and the purity of methane used in the test was 99.99%. Sodium dodecyl sulfate (SDS) was used as a surfactant to promote hydrate formation.

2.2. Methods of testing
The freezing point of drilling fluid was measured by step cooling curve method. The drilling fluid was cooled slowly in a low temperature incubator, and its temperature change was recorded by a temperature sensor. The temperature of drilling fluid first decreased, then stabilized for a period of time, and finally decreased. The stable temperature was the freezing point of drilling fluid.

The rheological properties of drilling fluid were measured by six-speed rotational viscometer. Apparent viscosity (AV), plastic viscosity (PV) and yield point (YP) were calculated from φ600 and φ300 readings (API RP13B) by the following formula:

\[
\text{apparent viscosity (AV)} = \frac{\phi 600}{2} \text{ (mPa} \cdot \text{s)} \\
\text{plastic viscosity (PV)} = \phi 600 - \phi 300 \text{ (mPa} \cdot \text{s)} \\
\text{yield point (YP)} = \frac{\phi 300 - PV}{2} \text{ (Pa)}
\]

The fluid filtration was measured by the medium pressure filtration meter. According to the standard procedure recommended by American Petroleum Institute, the drilling fluid filtration of 7min at 0.7MPa was tested.

The swelling ratio was measured by a linear dilatometer. 10 g samples were ground to 45 μm, and then added into a 25.4 mm diameter mould at 10 MPa for 5 min. The swelling height change of the test sample was recorded after contacting with the drilling fluid. When the growth ratio of swelling height was less than 0.01%, the swelling ratio was calculated.

Cuttings dispersion test was used to evaluate the dispersion inhibition of drilling fluid. 50g samples were ground and selected with the particle size between 2-4 mm. After rolling dispersion at room temperature for 16 hours, the samples were screened through a 0.425 mm sieve. And after washed, dried and weighed, the recovery ratio of shale dispersion was calculated.

The experiment of hydrate formation and decomposition was carried out by the experimental device of natural gas hydrate inhibition evaluation. The reactor was cleaned with deionized water, and then 500 mg/L SDS aqueous solution was added to the reactor to promote the formation of methane hydrate. Temperature was cooled by water bath system, and methane gas was injected after the temperature was stable. Methane hydrate was generated at a constant volume at 4 °C and 10 MPa. After the formation of hydrate, the horizontal flow pump was used to drive the drilling fluid into the reactor. And then the experiment of hydrate decomposition began with the increase of temperature. The change of temperature and pressure during the experiment was recorded. When the temperature change was less than 0.1 °C and the pressure change was less than 0.01 MPa within 30 min, the hydrate decomposition process was completed.

The biological toxicity test was to determine the half maximum effective concentration (EC₅₀) through the water toxicity test device. After the test solution was diluted, it was put into different experimental tanks, and luminescent bacteria were added respectively. Then the EC₅₀ value was calculated by detecting the luminous effect.
3. Results and discussions

3.1. Construction of environment-friendly drilling fluid system
Based on the treatment agent optimization and formulation optimization experiments, an environment-friendly drilling fluid system was formed by using NaCl as antifreeze, XC and SCH as anti-salt rheology regulators, CMS as filtration reducer, CC as plugging agent and PVP as double-effect hydrate inhibitor. Combined with the drilling requirements of hydrate formation, the orthogonal test was further carried out, and the specific proportion of environmental-friendly low-temperature water-based drilling fluid system was finally determined, as shown in Table 1.

| Component      | Concentration (%) |
|----------------|-------------------|
| Sodium Bentonite | 4%                |
| XC             | 0.1%              |
| SCH            | 0.3%              |
| CMS            | 0.15%             |
| CC             | 1%                |
| PVP            | 0.5%              |
| NaCl           | 15%               |

3.2. Rheology and filtration
As the simulated drilling temperature in offshore natural gas hydrate formations ranges from 4-30 ℃, the rheology and filtration properties of drilling fluid at 4 ℃, 15 ℃ and 30 ℃ are shown in Table 2. The freezing point of drilling fluid is -10 ℃ and it still has good rheology at 4 ℃. Plastic viscosity is controlled within 32.5 mPa·s and yield point 17 Pa. The apparent viscosity ratio (AV(4℃)/AV(30℃)) is less than 1.3. The dynamic plastic ratio is about 0.5, which is beneficial for wellbore cleaning. In addition, the filtration of the drilling fluid is 4 mL at 30 ℃, which shows good filtration.

| Freezing (℃) | Temp (℃) | AV (mPa·s) | PV (mPa·s) | YP (Pa) | FL(API) (mL) |
|--------------|----------|------------|------------|--------|--------------|
| -10          | 30       | 42.5       | 28.0       | 14.5   | 4.0          |
| -10          | 4        | 54.5       | 37.5       | 17.0   | 3.5          |

3.3. Shale inhibition performance
Shale hydration is an important factor causing wellbore instability. Therefore, drilling fluid is required to have a good ability to inhibit shale hydration and dispersion. Fig. 1 shows under room temperature, the swelling ratio of shale sample is 10.45% in fresh water, and 2.66% in drilling fluid, with the reduction rate of 75%. At 4 ℃, the swelling ratio is less than 2%, which indicates that the drilling fluid has good hydration inhibition. The results of dispersion test are shown in Figure 2. The recovery radio of different shale samples in fresh water are 33.4%-38.1%, but they are all higher than 90% in drilling fluid, which indicates that drilling fluid can effectively inhibit shale dispersion.
3.4. Hydrate inhibition performance

Drilling fluid for hydrate formation not only needs to meet the requirements of inhibiting the decomposition of hydrate in formation, but also needs to meet the requirements of inhibiting the formation of hydrate in wellbore. Fig. 3 shows that the temperature of the reactor remains stable and the pressure only drops by 0.3 MPa. This proves that there is no hydrate formation, indicating that the drilling fluid can effectively inhibit hydrate formation in wellbore. Peng-Robinson equation is used to calculate the change of mole number of methane gas produced by hydrate decomposition. And the experimental results are shown in Figure 4. Compared with the experimental fluid without hydrate decomposition inhibitor, the mole number of hydrate decomposition gas in the drilling fluid system increases slowly, and the equilibrium time of the system increases obviously, showing good performance of delaying hydrate decomposition.

\[
P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)}
\]

Where P is pressure, MPa; T is temperature, K; \(V_m\) is molar volume, L/mol; R is gas constant, 8.3145 J/(mol·K); \(a(T)\) is energy, which can be determined by critical parameter; b is covolume constant, which can be determined by eccentricity factor.

3.5. Environmental protection performance

Because of the high requirement of offshore ecological environment, it is necessary to use non-toxic drilling fluid. EC50 value measured by biological toxicity test is a common environmental protection index. The EC50 standard of drilling fluid that can be discharged is over 3×10^4, and the EC50 value of
the drilling fluid constructed in this paper is $4.2 \times 10^5$, which meets the discharge standard of drilling fluid in offshore and has high environmental protection performance.

4. Conclusions

The environment-friendly low-temperature water-based drilling fluid system for drilling hydrate formation is established through optimization of additives. Comprehensive evaluation results show that it has good rheology and filtration. The drilling fluid also can effectively inhibit shale hydration and maintain formation wellbore stability. Moreover, it can not only inhibit hydrate decomposition in formation, but also inhibit hydrate formation in wellbore. In addition, it also has good environmental protection performance. The drilling fluid system constructed in this paper provides environmental-friendly drilling fluid technical support for the exploration and development of hydrate formation in offshore.

Acknowledgments

The authors would like to acknowledge the financial support of the National Natural Science Foundation of China (Major Program, 51991363), CNPC’s Major Science and Technology Projects (ZD 2019- 184-003) and the Postgraduate Innovation Projects (YCX2020030).

References

[1] Sun Z, Wang R, Fan S and Guo K 2001 Natural Gas Industry 21 93-96
[2] Hu W 2010 Natural Gas Industry 30 1-8
[3] Kvenvolden K 1999 Proceedings of the National Academy of Sciences 96 3420-3426
[4] Milkov A V 2004 Earth-Science Reviews 66 183-197
[5] Ning F, Zhang K, Wu N, Zhang L, Li G, Jiang G, Yu Y, Liu L and Qin Y 2013 Geophysical journal international 193 1370-1384
[6] Liu T, Jiang G, Zhang P, Sun J, Sun H, Wang R and Zheng M 2016 Journal of Natural Gas Science and Engineering 33 934-941
[7] Charie V D, Sharma D V, Prasad P S R and Murthy S R 2013 Journal of Natural Gas Science and Engineering 11 7-11
[8] Freij-Ayoub R, Tan C, Clennell B, Tohidi B and Yang J 2007 Journal of Petroleum Science and Engineering 57 209-220
[9] Hao S 2011 Journal of Petroleum Science and Engineering 76 109-115
[10] Zhang Y, Qiu Z, Zhao X, Zhong H, Huang W and Mu J 2021 Polar Science 100645
[11] Khabibullin T, Falcone G and Teodorici C 2011 SPE Drilling & Completion 26 287-294
[12] Brown T D, Taylor C E and Bernardo M P 2010 Energies 3 1154-1175
[13] Circone S, Stern L A and Kirby S H 2004 American Mineralogist 89 1992-1201
[14] Boswell R and Collett TS 2010 Energy Environment Science 4 1206-1215
[15] Akerman H J and Johansson M 2008 Permafrost and Periglacial Processes 19 279-292