Experimental Study on Inhibition of Hydrate Formation by Compound Solution of PVP and Ethylene Glycol Ether

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Abstract. Kinetic inhibitor is an inhibitor of many studies in the field of natural gas hydrate inhibitor in recent years. In view of the inhibition of hydrate effect is obvious, high cost, so this paper carried out several inhibitors to inhibit the formation of gas hydrate, in order to meet the need of gas hydrate inhibition, but also take the economic factor into account. It was found that the synergistic effect of PVP and ethylene glycol two ether, ethylene glycol two ether and ethylene glycol phenyl ether in the inhibition of gas hydrate, and the synergistic effect of ethylene glycol phenyl ether was the most significant.

Keywords: Natural gas hydrate; kinetic inhibitor; PVP.

1. Introduction
In recent years, low-dose new kinetic inhibitors have been studied to replace thermodynamic inhibitors at home and abroad. Kinetic inhibitors delay the growth and aggregation of hydrate crystals by prolonging the induction time of hydrate nucleation or changing the process of crystal aggregation, so as to achieve the effect of inhibiting hydrate formation¹⁻³. In view of the obvious effect of some inhibitors in inhibiting hydrate formation, but the high cost of use, this paper carried out experimental studies on the inhibition of hydrate formation by several inhibitors combined use⁴⁻⁶.

2. Experimental Scheme and Equipment
The experimental equipment is an evaluation system of inhibiting effect of natural gas hydrate inhibitor, which mainly includes reaction kettle, gas injection and injection pipeline, constant pressure and constant speed pump, temperature and pressure sensor, mass flowmeter, data acquisition system and so on.
Figure 1. Natural gas hydrate experimental flow.

The main technical parameters are shown in the table below.

Table 1. Main parameters of equipment for hydrate formation/inhibition experimental system.

| Performance parameters                  |          |
|-----------------------------------------|----------|
| Working pressure                        | 20MPa    |
| working temperature                     | -15°C--100°C |
| Reactor Volume                          | 600ml    |
| Agitation speed                         | 0-600r/min|

In this experiment, polyvinylpyrrolidone (PVP) was mixed with different ethylene glycol ether solutions to develop the effects of different hydrate inhibitor systems. The ratio of reagents and reaction conditions were changed during the experiment, in order to select the most obvious inhibitory reagent formula for hydrate formation.

3. Inhibition of Hydrate Formation by polyvinylpyrrolidone (PVP)

Hydrate formation experiments of polyvinylpyrrolidone (PVP) with 0.5% and 1% mass fractions were carried out under simulated water depth of 1200 meters. The data of temperature and pressure varying with time were collected during the experiment, and the formation diagram of PVP hydrate was obtained as shown in the following figure. The experimental results show that the inhibiting effect of 0.5% PVP on hydrate is not as good as that of 1% PVP.

Figure 2. Molecular structure of PVP.
Figure 3. 0.5% mass fraction polyvinylpyrrolidone (PVP) hydrate formation diagram.

Figure 4. A schematic diagram of hydrate formation of polyvinylpyrrolidone (PVP) with a mass fraction of 1%.

PVP can inhibit the nucleation and growth of hydrate to some extent, but the inhibition effect is limited in the simulated 1200 water depth, high pressure and low temperature environment withstanding 6 degree of supercooling. PVP can reduce the dissolution rate of gas and prolong the induction time of hydrate formation. Moreover, PVP molecules can form hydrogen bonds between oxygen atoms in the five-membered ring structure and hydrate surface to hinder the growth of hydrate crystals. PVP molecular structure can be adsorbed on the surface of hydrate molecules to form porous membranes, which can effectively prevent hydrate and methane from entering into one. Step-by-step contact inhibits hydrate growth.

4. Inhibitory Experiments of polyvinylpyrrolidone (PVP) and Different Ethylene Glycol Ethers, Respectively

The kinetics inhibitor PVP was used as the main agent of compound inhibitor, and ethylene glycol dimethyl ether, ethylene glycol diethyl ether and ethylene glycol phenyl ether were added as synergist to prepare compound inhibitor.

Figure 5. Molecular structure diagram of synergist.
Fig. 6-8 shows the inhibition time of different complex inhibitors on hydrate. It can be seen from the graph that the inhibition performance of PVP and ethylene glycol phenyl ether is the best, the inhibition performance of ethylene glycol dimethyl ether is relatively weak, and the inhibition performance of ethylene glycol diethyl ether is the weakest. The inhibition time of the three synergists on hydrate formation is different. For example, when the dosage of ethylene glycol phenyl ether is 0.5% (w), the inhibition performance is weak, the induction time of hydrate formation is less than 10 minutes; when the dosage of ethylene glycol phenyl ether is 1.5% (w), the supercooling temperature of 5 under the initial temperature and pressure is withstood, and no hydrate formation is found after 840 minutes. The experimental results show that ethylene glycol phenyl ether can effectively inhibit hydrate formation.

**Figure 6.** Inhibitory experiments of 1% mass fraction PVP and 1.5% mass fraction ethylene glycol dimethyl ether.

**Figure 7.** Inhibition experiments of 1% mass fraction PVP and 1.5% mass fraction ethylene glycol diethyl ether.
Figure 8. Inhibitory experiments of 1% mass fraction PVP and 1.5% mass fraction ethylene glycol phenyl ether.

Table 2. Inhibition of PVP Compound Inhibitors on Hydrates Formation of compounds.

| Main agent | Synergist mass fraction % | Induction time /min | Supercooling /°C |
|------------|--------------------------|---------------------|------------------|
| PVP 1      | Ethylene glycol dimethyl ether 1.5 | 370                | 6                |
| PVP 1      | Ethylene glycol diethyl ether 1.5 | 212                | 6                |
| PVP 1      | Ethylene glycol phenyl ether 1.5 | 370                | 6                |

5. Conclusion

Under certain supercooling conditions, the kinetic inhibitor PVP could not significantly inhibit the nucleation of hydrate, but could prolong the growth time of hydrate. It indicated that the hydrate inhibitor with lactam group as the key group mainly inhibited the growth of hydrate by delaying the growth of hydrate and compounded with ethylene glycol ether. The inhibitory effect of combined inhibitors was better than that of PVP alone, and the inhibitory effect of ethylene glycol phenyl ether was better than that of ethylene glycol dimethyl ether and ethylene glycol diethyl ether.

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