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Formation and Prevention of Natural Gas Hydrates

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Abstract
Natural gas hydrate is formed under certain temperatures and pressures, which makes it an unavailable clean energy source. However, in industrial production, clogging occurring due to hydrate generation can cause a series of safety accidents and economic losses. In order to solve the hazards of natural gas hydrates in drilling, this paper reviews the formation conditions of natural gas hydrates and the prevention and control measures. In order to inhibit the formation of hydrates, the use of traditional well control measures and the addition of thermodynamic inhibitors have high costs, large dosages, an unfriendly environment, etc. The new type of kinetic inhibitor has a strong effect and low dosage and is considered to be the most promising chemical treatment for hydrate prevention and control in the industry. However, kinetic inhibitors are greatly affected by environmental factors, and compounding them with thermodynamic inhibitors and their synergistic effect can greatly reduce the dosage of thermodynamic inhibitors and improve inhibition performance. It is an important direction for laboratory research and has shown good results in field applications.

Keywords: gas hydrate; deep-water; drill; prevention and cure; kinetic inhibitors

1. Introduction

Natural gas hydrates, also known as combustible ice, are non-stoichiometric cage-like crystalline solid compounds formed by natural gas molecules at high pressure and low temperature through weak intermolecular forces [1-2]. Large quantities of in situ gas hydrates are present in the deep ocean and permafrost zones, and about 97% of seafloor hydrate deposits [3-5]. Due to the abundant reserves and high energy density, it is considered one of the most promising clean energy sources after coalbed methane, tight gas, and shale gas [6,7]. Using seismic tagging, sampling, logging, and biological or carbonate crustal tagging, hundreds of natural gas hydrate production sites have been discovered around the world [8,9]. It has been found that gas hydrate-bearing areas are mainly located in high-latitude or high-elevation perennial permafrost zones, as well as in geological environments such as accretionary wedges along active continental margins, and cold-geyser vents, mounds, faults, mud volcanoes, and sumps along passive continental margins [10-12]. The global in situ resource of gas hydrates is estimated to be about $3 \times 10^{15} m^3$ [13], which is 1.56 times the total known natural gas reserves [14]. If commercial extraction of natural gas is realized, it could be even more revolutionary than the shale gas revolution, which would have a huge impact on the energy market. Over the past three decades, gas hydrates have become an increasingly important aspect of global energy strategy. Several countries and regions, including the United States, Canada, Japan, China, Russia, South Korea, India, and the European Union, have developed hydrate research programs and conducted extensive exploration, identification, drilling, coring, and actual production tests [15,16].

However, from another perspective, natural gas hydrates can pose a threat to already fragile climate and environmental systems if large-scale, accidental releases of methane gas from hydrate reservoirs occur [17]. Hydrates are also considered industrial hazards in the extraction sector of the natural gas industry, as clogging due to the formation of hydrates in oil and gas pipelines or drilling fluids can lead to unplanned production shutdowns and unsustainable economic losses [18,19]. Therefore, prevention and remediation management strategies for gas hydrates are challenging and important. Even in deep-sea hydrate exploration practices, including trial production of natural gas from hydrate reservoirs, the risk of hydrate clogging in drilling fluids will inevitably be faced due to the harsh conditions of colder seawater, higher pressures, and lower temperatures on the seafloor.

2. Formation and importance of hydrates

Natural gas hydrates are formed in two forms: as a naturally occurring phenomenon, and as an industrial activity ‘technological gas hydrates’ formed in technological systems created and controlled by humans [20]. Szamałek's research shows that the first reported natural gas hydrates were produced by Humphrey Davy in 1810 under laboratory conditions. On the other hand, the first formation of hydrates in the oil and gas system was discovered in 1934 by the American chemist E.G. Hammerschmidt, who found that methane hydrates in frozen ice impeded the flow of gas in the Russian gas pipeline [21]. The presence of hydrates in natural geological conditions reported by Szamałek in 2004 was not reported until 1967 in the Siberian Messiyakhi oil and gas field and was confirmed only during the exploration work. Usually, gas hydrates are found in permafrost and on the seabed, and some of these compounds are found in outer space [22].

In general, the formation and stabilization of hydrates in sediments require the following conditions:

1. The presence of free water is necessary for hydrate formation.
2. Suitable thermodynamic conditions, including low temperature and high pressure.
3. The presence of sufficient quantities of thermogenic biogenic or non-hydrocarbon hydrocarbon gases, such as H_2S and CO_2, which are mainly supplied by subsurface sediments or bacteria [23-25].
4. Flow pattern. Studies have shown that hydrodynamic segment plug flow increases the rate of hydrate formation at the head of the segment plug. This is due to the presence of a large gas-water interface area at this location.
5. Other factors such as solid impurities, rough pipe walls, high-speed churning, or pressure fluctuations, in short, turbulence is considered a catalyst for hydrate formation.

Since the formation and stabilization of gaseous hydrates require special thermodynamic conditions, these compounds are found in two geological regions. One is at high latitudes and at depths of less than one to two kilometers, where temperatures are lower and also above zero degrees Celsius, and the second is in the depths of the oceans and deep lakes, as well as in low-temperature, high-pressure sediments on continental slopes and deep in the oceans [26-28]. Currently, natural gas hydrates are receiving a lot of attention from researchers and the scientific community because of their great potential.

The importance of natural gas hydrates can be summarised as follows:

1. Natural gas hydrates will be the world's fuel supplier in the coming years [29].
2. Clogging of gas pipelines and gas wells.
3. Drilling hazards, clogging of gas pipes, conduits, water traps subsea blowout preventers, etc.
4. Seabed instability [30].
5. The greenhouse effect of gases in hydrate structures and increase in global temperature.

3. Prevention and control of hydrates

The formation of gas hydrates and their potential clogging in petroleum transport systems has attracted widespread attention from academia and industry as a major safety hazard. In deepwater operations, the low-temperature and high-pressure environment of the seafloor fuels the formation of hydrates, and once natural gas hydrates are formed in the throttling lines, drilling watertight conduits, blowout preventers, and subsea wellheads, clogging occurs, which can have a serious impact on normal drilling and well control work. The following are the main preventive and control measures for hydrates.

3.1. Use of low-density drilling fluids and good well control measures

Hydrates are formed under a certain temperature and pressure, and it is not practical to increase the temperature of the drilling fluid at the seafloor, so the pressure in the wellbore can be controlled by adjusting the density of the drilling fluid, and maintaining the lowest safe drilling fluid density helps to prevent the formation of hydrates 31. However, the drilling fluid density cannot be too low according to the formation conditions and the drilling depth, so it is not desirable to control hydrate formation only by adjusting the drilling fluid density. In addition, hydrate formation occurs only when natural gas enters the wellbore, and it is not easy to form hydrates as long as good well control measures are implemented.

3.2. Oil-based drilling fluids

Oil-based drilling fluids are less likely to form hydrates, which are easily formed when the water content exceeds 20 percent. The use of oil-based drilling fluids reduces the amount of free water in the drilling fluid, thus preventing the formation of hydrates. All oil drilling fluids must be used, otherwise, hydrate formation is still possible in deepwater offshore drilling. The use of oil-based drilling fluids makes it easy to control the formation of gas hydrates, but the cost of oil-based drilling fluids is too high and the recovery process is complicated, so the promotion of oil-based drilling fluids is limited.

3.3. Chemical inhibitor

In addition to the above measures, the most commonly used is the addition of chemical treatment agents to the drilling fluid. Chemical treatment agents can be divided into thermodynamic inhibitors, kinetic inhibitors, and anti-aggregation agents.

(1) Thermodynamic inhibitors

Thermodynamic inhibitors (THIs) are alcohols and inorganic salt inhibitors, including methanol, ethylene glycol, isopropanol, diethylene glycol, ammonia, calcium chloride, etc. The mechanism is that through the competitiveness between inhibitor molecules and water molecules, it can change the chemical potential of the aqueous solution or the hydrate phase, change the thermodynamic equilibrium conditions between the water and gas molecules, and make the decomposition curve of the hydrate move to the lower temperature or the higher pressure, thus achieving the purpose of promoting the decomposition of hydrate. The purpose of inducing hydrate decomposition [31]. However, in the case of methanol or MEG, for example, they may require as much as 20 wt%-60 wt% for effective inhibition, and instead of having an inhibitory effect, low concentrations of thermodynamic inhibitors may actually even promote hydrate formation and growth. The use of alcohols and salts also faces challenges such as high volatility, the need for large storage capacity and recovery devices, strong corrosion of tube walls, and environmental unfriendliness. Cost implications, quantity of chemicals required, health, safety, and environmental suitability, as well as deployment issues, may be critical in the selection of an effective THI inhibitor.

Studies have shown that as production from offshore gas wells moves into colder and deeper zones, conventional methods using THIs face challenges such as high injection rates and large storage requirements.

To address these challenges and inconveniences, low-dose hydrate inhibitors (LDHIs) have been explored in depth. Low-dose hydrate inhibitors (LDHIs) are used at significantly lower concentrations compared to thermodynamic inhibitors. These inhibitors either prevent the formation or growth of hydrate crystals. Based on different studies, LDHIs are divided into two categories; kinetic hydrate inhibitors (KHIs) and anti-aggregation agents (AAs).

(2) Kinetic inhibitors

Kinetic hydrate inhibitors (KHIs) are defined in relation to conventional thermodynamic inhibitors based on their antichemical effect on hydrate nucleation and growth, and refer to a number of water-soluble or water-dispersible polymers, these include homopolymers and copolymers of n-vinylpyridone and n-vinylcaprolactam. They inhibit hydrate generation by significantly reducing the rate of hydrate nucleation, delaying or even preventing the generation of critical nuclei, interfering with the preferred growth direction of hydrate crystals, and affecting the orientational stability of hydrate crystals. In the early stage of hydrate nucleation and growth, the dynamic inhibitors are adsorbed on the surface of hydrate particles, and the cyclic structure of the active agent binds to the hydrate crystals through hydrogen bonding, thus preventing and delaying the further growth of hydrate crystals [31]. It was found that the addition of a small amount of dynamic inhibitor will change the growth habit of structural Π hydrate, and the addition of inhibitor to structure I will cause rapid partitioning of crystals. At higher inhibitor concentrations, the growth stopped for both structure I and Π crystals. Ruoff and Lekvam studied the whole process of kinetic inhibitor action and classified the hydrate generation process into the nucleation stage, slow growth stage, and fast growth stage. Kinetic inhibitors should focus on inhibiting the rapid growth phase of hydrates [32].

The molecular chain of polymer-based inhibitors is characterized by a large number of water-soluble genes and long aliphatic carbon chains, and their mechanism of action is to inhibit hydrate formation by preventing the growth of hydrate nuclei through eutectic or adsorption or by keeping hydrate particles dispersed without aggregation. From the application status quo, polymer-based inhibitors are less dosage, more widely used, and more environmentally friendly, but the disadvantage is that they are greatly affected by environmental factors and are prone to inhibition failure at high supercooling.

(3) Anti-Aggregating Agents

Anti-aggregating agents (AAs) are mostly polymers and surfactants. Surfactants that can be used as anti-aggregation agents include alkyl aromatic sulfonates and alkyl polyglycosides, and Urdahr et al. proposed the use of surfactants such as alkyl ethoxy phenyl compounds as anti-aggregation agents. Antipolymerisation agents include alkyl aryl sulfonates, alkyl glycolated alkyl phenyl hydroxyethyl salts, tetraethoxylates, and bile acids (e.g., glycosidic oil bile acids). The mechanism of action is to change the size of the hydrate crystals and alter the aggregation pattern by adsorption of inhibitor molecules onto the hydrate cage [33,34]. Usually, the anti-aggregation effect is not as dependent on the magnitude of subcooling as in the case of kinetic inhibitors, so they are applied over a wider range of temperatures and pressures.

Disadvantages of hydrate antipolymerisation agents: limited dispersive properties, prevention of gas hydrate formation only when oil and water coexist, and the effect is related to the water content of the oil phase composition and the salt content of the water phase, i.e., the antipolymerisation agent has a mutual selectivity with the oil and gas system.

(4) Combined inhibitors of KHIs and THIs

The inhibition mechanism of THIs on natural gas is to change the thermodynamic conditions of the system, which is completely outside the phase equilibrium region of hydrate generation, and the addition of THIs can make the supercooling degree of KHIs decrease, so that KHIs can play the inhibitory performance under a lower supercooling degree. Therefore, in the field application of KHIs, THIs are often added in combination to achieve a better inhibition effect. There are examples of good inhibition effects achieved by combining THIs and KHIs. Lee et al. combined polyethylene glycol (PEG) with eight types of KHIs and found that the inhibitors could prolong the induction time of hydrate generation after the combination. The reason for this is that THIs can change the thermodynamic conditions of the gas-liquid system, and the KHIs delay the hydrate nucleation and growth under conditions more suitable for them to exert their inhibitory effects, thus acting to inhibit the growth of hydrates [35-37]. Tang Cuiping and Dai Xingxue used ether alcohols in combination with polyether amines and KHIs and found that the combined inhibitors performed better than commercial inhibitors such as Inhibex501. In addition, other researchers used KHIs in combination with salts to explore their synergistic inhibition [38]. In field applications, such as the Green Valley Super 2000m in the Gulf of Mexico and 2500m in North Texas, USA, where KHIs were used in synergistic inhibition with THIs, the generation of hydrates was better inhibited.

4. Conclusion

Natural gas hydrates are formed under certain environmental conditions, such as pressure and temperature, and are a huge source of fuel supply. However, a series of safety issues may arise once excessive hydrates are formed in the equipment during drilling work. At this stage, a more in-depth study on the formation mechanism of hydrates is needed, which is conducive to finding more targeted inhibition measures. Before implementing drilling operations in deepwater areas, the possibility of gas hydrate formation in wellheads, blowout preventers, throttling and pressure lines should be considered comprehensively, and more importantly, important information parameters such as temperature, pressure, and composition of the gas and liquid phases should be measured.

(1) The presence of free water, a certain low temperature and high pressure environment and the supply of natural gas gas are necessary conditions for the formation of natural gas hydrates. The presence of some other solid impurities, rough pipe walls, high-speed churning or pressure fluctuations have a catalytic effect on hydrate generation and growth.

(2) In deepwater drilling operations, the response to gas hydrate formation is very important. The use of low-density or oil-based drilling fluids can well inhibit the generation of hydrates, but the implementability is poor and the cost is too high; the industry's main practice is to add hydrate inhibitors to the drilling fluid, so that the drilling fluid in a variety of conditions can still prevent hydrate formation, additives to inhibit the formation of hydrates can be divided into three major categories: thermodynamic inhibitors, kinetic inhibitors, and antiaggregating agents.

(3) Thermodynamic inhibitors have strong effects, but the dosage is large and the environment is unfriendly; anti-aggregation agents can cope with a wide range of temperatures and pressures, but they are mutually selective with the oil and gas system; kinetic inhibitors have a small dosage and are environmentally friendly, but they are greatly affected by

the environment and are difficult to cope with the situation of large supercooling. The combination of thermodynamic and kinetic inhibitors can greatly improve the inhibition performance, and different compounding combinations are being studied in various laboratories and show superior results in field applications.

(4) The prevention and control of natural gas hydrate should be based on the actual situation, a detailed understanding of the site conditions, a combination of methods, and choose to add effective hydrate inhibitors to inhibit the formation of hydrates in the extraction process.

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