

Research Article

## Natural Gas Hydrate Exploitation Technology Summarize

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**Abstract:** Gas hydrate, as a new energy source, has drawn extensive attention from the government, the companies and universities, and they have set up the related research department and the new Institute to strengthen the research of the hydrate. The development of the hydrate has also become a hot spot. The basic idea of natural gas hydrate exploration is to consider how to make the gas hydrate in the sediment to be decomposed, and then exploit the natural gas to the ground. In general, it is the main idea to break down the temperature and pressure conditions of natural gas hydrate stability, that is, the phase equilibrium condition, which causes the decomposition of gas hydrate. This paper introduces four kinds of common mining methods: thermoelectro-liminesence method, pressure reduction release method, inhibitor method, gas substitution method.

**Keywords:** Gas hydrate; Thermoelectro-liminesence; Pressure reduction release; Inhibitor; Gas substitution.

### INTRODUCTION

Natural gas hydrates, as a new source of energy, have attracted widespread attention from governments, major corporations and institutions of higher learning, and they have set up research institutes and new colleges to strengthen hydrate research. The development of hydrates has also become a hot spot. Natural gas hydrate, referred to as hydrate, also known as "combustible ice", is formed by water and natural gas in high temperature and low temperature environment,

the formation of ice, crystalline cage compounds (Figure 1). Natural gas hydrates are mainly distributed in deepwater (> 300m) marine subterranean and permafrost zones. Gas hydrates are often dominated by methane hydrate. The gas of the envelopes is mainly methane and is very similar to that of natural gas. This compound With a small molecular weight, chemical composition is unstable. The molecular formula is  $MnH_2O$ .



Fig-1 Natural gas hydrate sample

The basic idea of natural gas hydrate extraction is to first consider how to separate the gas hydrate stored in the sediments and then take natural gas to the ground. In general, it is the main idea to exploit the natural gas resources in natural gas hydrate by

artificially breaking the temperature and pressure conditions of gas hydrate stability, that is, the phase equilibrium condition and causing its decomposition.

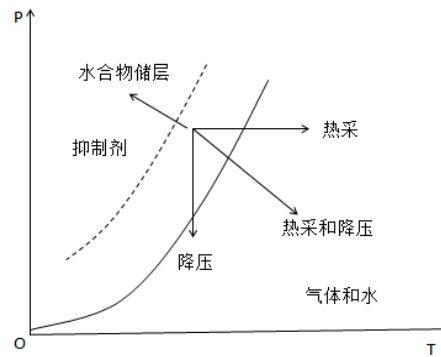
**NATURAL GAS HYDRATE DEVELOPMENT METHOD**

**Hydrate thermal excitation mining**

**1. Thermal excitation technology principle**

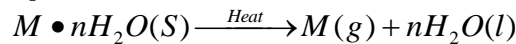
The pyrolysis of natural gas hydrate is a method of directly supplying reservoir heat from an external environment other than hydrate reservoirs, such as injecting hot water, to increase the temperature of the hydrate reservoir, So that the hydrate

decomposition, and then the gas mining program. This method of mining than the buck method and chemical reagent method has a direct heat, the effect of rapid, hydrate decomposition effect is obvious; the other can control the heating position, so that the reservoir can be achieved in the case of heat to meet the demand .And has the advantages of small environmental impact, suitable for a variety of different storage characteristics (Figure 2).



**Fig-2: Natural gas hydrate phase diagram**

The decomposition of this mining method is as follows: M is a gas molecule, s is solid, g is gaseous, l is liquid.



At present, thermal mining technology includes hot water/steam/hot water, underground heating/burning, the use of submarine geothermal, electromagnetic heating, microwave heat

conduction, solar heating and so on. According to the different ways of heat can be further divided into two categories:

- ① Heat from the surface into the hydrate reservoir, such as steam injection, hot water / hot salt water;
- ② Heat in the underground hydrate reservoir directly to provide, such as electromagnetic heating, underground combustion.

**Table 1: Advantages and disadvantages of different thermal mining methods**

method	advantage	Disadvantages
Injection of hot fluid (hot water, brine)	Simple and recyclable	Low efficiency, a lot of heat loss
Electromagnetic heating	Heating quickly, easy to control	Requires a lot of energy sources and complex equipment
Microwave heating	Easy to control, through the waveguide transmission	Lack of high power magnetron
Solar heating	Efficient, clean, non-polluting	Susceptible to climate change

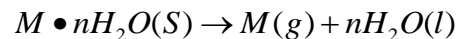
**Hydrate buck production**

**1. The principle of reduce pressure mining technology**

The reduction of pressure is one of the main methods of natural gas hydrate extraction. Is to reduce the pressure of the gas hydrate reservoir by pumping action, which is lower than the equilibrium pressure of the hydrate under the temperature condition of the region, so that the hydrate produces the methane gas from the solid decomposition phase change.

Methane gas and water to form hydrate and hydrate decomposition of methane gas and water

chemical reaction equation is as follows, M for the gas molecules, s is solid, g is gaseous, l is liquid.



The methane gas molecules in the porous media of the formation will be bound to the water molecules when the formation pressure rises or the temperature decreases, Through the combination of van der Waals force into a solid shape of the hydrate [1]. When the formation pressure is reduced or the temperature rises, the reaction proceeds to the left, where the van der Waals force decreases between the

methane gas molecules and the water molecules, and the solid hydrate structure releases a large amount of methane gas molecules. Thus, the extraction of natural gas from the strata that has formed the gas hydrate is, in effect, the decomposition of the gas hydrate, the decomposition of the hydrate. The depressurization method is a measure to promote the decomposition of the hydrate.

When the bottom of the hydrate deposit and the cap layer are non-permeable layer, in a production well can be drilled through the cap layer to reach the hydrate layer, then reduce the bottom hole pressure can hydrate the stability of the state damage, the final hydrate decomposition, Continuous generation of gas. Because this type of hydrate deposits in the initial buck area is limited, may lead to lower initial gas production rate. With the hydrate decomposition, the decomposition surface will continue to increase, gas production rate will be improved. In order to improve the initial gas production rate, you can first by injection or injection of chemical reagents in the bottom of the formation of a larger natural gas "capsule" to increase the area of unstable hydrate, improve gas production speed [2].

Under suitable conditions, natural gas hydrates and gas reservoirs are often associated with the natural gas hydrate layer because of its low permeability can be used as a natural gas reservoir cap closed natural gas. At this point, the hydrate layer can be drilled in the production well to reach the free gas reservoir, and the reservoir pressure is reduced by exploiting the free gas below the hydrate layer so that the hydrate in contact with the natural gas is unstable and decomposed.

## 2. Features of antihypertensive mining

The design of the depressurization method is similar to that of conventional oil and gas exploration, and the pressure in the hydrate is very fast. The extraction of free gas under the hydrate layer is one of the effective ways to reduce the reservoir pressure. In addition, the regulation of the pressure of natural gas can achieve the purpose of controlling the reservoir pressure and the effect of controlling the decomposition of hydrate. The buck method does not require expensive continuous excitation. Therefore, the buck method is a great potential for economic and effective mining. And its shortcomings mainly include:

(1) the production process must be the production speed and pressure for fine control, intermittently to provide heat for the formation;

(2) need to be equipped with artificial lifting equipment and production of water collection and treatment equipment, and develop strict sand control measures;

(3) drilling logistics and operating costs are huge, wellbore and gathering and transportation equipment must take measures to protect the flow;

So need to cycle heating, mechanical lift, chemical production and many other methods of integration.

## Hydrate inhibitor preparation

### 1. Hydrate inhibitor principle

By adding chemical inhibitors (including brine, methanol, ethanol, ethylene glycol, glycerol, etc.), can change the phase equilibrium conditions of hydrate formation, reduce the stability of hydrate temperature, change the gas hydrate stability zone regulator conditions, Resulting in the decomposition of some of the gas hydrate.

When the inhibitor is added, the phase equilibrium curve is shifted left and the reaction proceeds to the right. Methane gas molecules and water molecules between the van der Waals force weakened, the solid shape of the hydrate structure will release a large number of methane gas molecules. Thus, the extraction of natural gas from the strata that has formed the gas hydrate is, in fact, the decomposition of the gas hydrate, the hydrate decomposition process; the "inhibitor" inhibits the formation of the hydrate, which in effect promotes the hydrate dissociation, Which in turn enables us to mine natural gas. Therefore, hydrate inhibitors, in addition to the field can be used in hydrate mining, drilling fluid by adding hydrate inhibitors is also deepwater drilling operations hydrate control widely used.

Hydrate inhibitors have the advantage of reducing the initial energy input, but the addition of chemical inhibitors is slower than the heating method, which is expensive and does not apply to commercial applications and is liable to cause environmental pollution. Seabed hydrate pressure is high and therefore should not be large-scale use of hydrate inhibitors, need to combine the use of other means of mining.

### 2. The type of inhibitor

Adding the inhibitor to the pipeline can change the rate of nucleation and aggregation of the hydrate, reduce the formation temperature of the hydrate and increase the pressure in the normal flow of the fluid, and change the critical point of the hydrate factor Inhibition of hydrate production, the main types of inhibitors are thermodynamic inhibitors, kinetic inhibitors, anti-polymerization agent.

#### (1) Mechanism of thermodynamic inhibitor (THI)

The use of water molecules and inhibitors of molecular or ionic competition between the role of change to change the thermodynamic equilibrium

conditions, so that the pressure and temperature in the practical application conditions, to prevent the hydrate production or let it contact with the hydrate, so phase balance The curve changes, making the hydrate structure can not stabilize the state, so as to achieve the purpose of decomposition of hydrate.

**(2) Kinetic inhibitor (KHI) mechanism of action**

Kinetic inhibitors are used to slow down the rate of hydrate nucleation, slow down the rate of its formation, interfere with the growth direction of its crystal and other columns to inhibit the formation of hydrate. It is generally a water-soluble or water-dispersible polymer, generally in the aqueous phase of the kinetic inhibitor to play a inhibitory effect, when the injection concentration is low, hydrate formation thermodynamic conditions will not be affected. In the early stages of hydrate production and growth, they adhere to the surface of the hydrate crystals, hydrate crystals and the hydrogen bonds of the inhibitors, thus suppressing their nucleation times or preventing the growth of nuclei, thereby reducing The formation of hydrates in the pipeline to promote the decomposition of hydrate, so that the pipeline smooth, reduce losses [4].

**(3) Anti-polymerization agent (AA) mechanism of action**

Anti-polymerization agent and other inhibitors of the mechanism of action is different, which is mainly played the role of emulsification, equivalent to the polymer and surfactant, if both the presence of oil and water can be used in order to play a inhibitory effect The Adding a certain amount of anti-polymerization agent to the system will be able to emulsify the oil and water phase, the oil can be dispersed into a lot of water droplets, even if the oil phase dispersed in the water

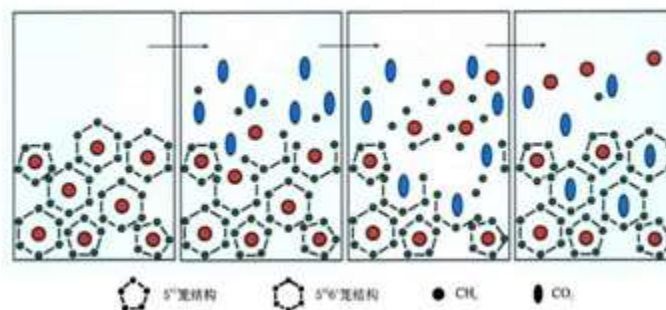
droplets and gas hydrate, but the hydrate Was solubilized in microemulsion, it is difficult to gather into pieces, blocking the situation is difficult to happen. So the anti-polymerization agent in the pipeline closed or undercooled relatively large conditions have a very good inhibitory effect.

The shortcomings of the first three kinds of mining methods are mainly manifested in the low heat transfer efficiency of the formation, which limits the decomposition efficiency of the hydrate, which is due to the fact that the hydrate dissociation absorbs a large amount of heat and the poor thermal conductivity of the formation makes the temperature of the hydrate decomposition area can not be quickly compensated , So the effect of low efficiency. In addition, these three methods are based on the principle of decomposition of hydrate, will cause the hydrate layer strength decreases, and further bring the slope instability, damage to the sea and other environmental problems. Therefore, CO2 replacement of hydrates is gradually becoming the focus of the study of scientists [3].

**Gas exchange of gas**

**1. CO<sub>2</sub> replacement method for the introduction of hydrates**

This technique converts CH<sub>4</sub> molecules from the hydrate by introducing another guest molecule CO<sub>2</sub> into the gas hydrate and reducing the partial pressure of the CH<sub>4</sub> molecule in the hydrate phase to achieve the purpose of mining CH<sub>4</sub>. Since the displacement reaction occurs directly in the hydrate phase, the different guest molecules are exchanged without changing the structure of the hydrate. Therefore, the replacement technology does not cause geological hazards, so it can effectively control the safety hazard.



**Fig-3: Schematic diagram of CH<sub>4</sub> molecules in CO<sub>2</sub> gas exchange gas hydrate**

**2.Mechanism and Analysis of Displacement Mining**

The replacement mechanism is shown in Figure 3 below. CO<sub>2</sub> molecules through the van der Waals force will be surrounded by CH<sub>4</sub> gas molecules in the watercrows around the water molecules to attract over the original wrapped in CH<sub>4</sub> gas molecules around the water molecules in the water molecules between the

hydrogen bonds break, the formation of free water molecules, At the same time as more and more water molecules in the water cage to leave, had been "trapped" in which the CH<sub>4</sub> gas molecules were "released" out, the molecule will invade the already damaged cage structure affect the surrounding state of existence Intact molecular cage structure. As more and

more cage structures participate in the same process, a large number of CH<sub>4</sub> gas molecules are released.

With the release of CH<sub>4</sub> molecules, CO<sub>2</sub> molecules gradually in the damaged cage structure through the van der Waals force to attract free water molecules, and cage body re-"build" up, in the process of reshaping cage body, CO<sub>2</sub> Water molecules through the spatial structure of the change to achieve a balance of the lowest energy state, the excess energy released in the form of heat, so that the surrounding CH<sub>4</sub> hydrate cage body further decomposition, completed the replacement reaction process [5]. With the gradual change of the substitution reaction, the CH<sub>4</sub> molecules in the larger cage (51262 structure) are completely replaced, and the smaller CH<sub>4</sub> hydrate cage (512 structure) has a higher hydrogen bond force and van der Waals force, The energy of the CO<sub>2</sub> molecule can not be decomposed and the replacement reaction terminates. Nearly 30% of the CH<sub>4</sub> can not be replaced in the experiment.

In the CO<sub>2</sub> replacement method, the endotherm of the CH<sub>4</sub> hydrate decomposition process is complementary to the exotherm of the CO<sub>2</sub> hydrate formation process. The formation of the CO<sub>2</sub> hydrate after the decomposition of the gas hydrate is achieved by the compensation of the heat. The secondary formation of the hydrate is maintained Stratigraphic stability. In addition, through the CO<sub>2</sub> replacement method to achieve the greenhouse gas in the form of hydrate storage in the ground.

However, the exchange rate of CH<sub>4</sub> hydrate is usually very low, and some studies suggest the use of CO<sub>2</sub> + N<sub>2</sub> mixed gas for hydrate replacement, but studies [6] show that the introduction of N<sub>2</sub> increases the degree of substitution, but reduces the rate of substitution because the mixed hydration The addition of small molecule N<sub>2</sub> increases the filling degree of hydrate cage and reduces the diffusion rate of gas molecules. According to domestic and foreign scholars reported that the emulsion state of CO<sub>2</sub> showed a high CH<sub>4</sub> replacement rate, but in the preparation of CO<sub>2</sub> emulsion need to use surfactant (stabilizer) and vigorous stirring, which to some extent make the mining process Complex; in addition the emulsion contains larger dispersed particles, which can only pass through the formation of large pores and cracks, and hydrate formation is usually very low permeability, so show a great penetration resistance, so the CH<sub>4</sub> hydrate replacement Gaseous CO<sub>2</sub> is more effective than liquid or emulsion conditions.

## CONCLUSION AND OUTLOOK

(1) The comprehensive application of thermal excitation and depressurization is a more economical method for the exploitation of hydrate deposits. The thermal

excitation method has a long way to go to solve its heat utilization efficiency. The current local heating is not conducive to the large-scale exploitation of the hydrate reservoir. The antihypertensive method has obvious limitation on the hydrate reservoir itself, Is a technology suitable for large-scale mining.

(2) hydrate inhibitor method is a common method of mining in a weak method, can reduce the initial input energy, but its role is slow, the cost is too high. Thus, the hydrate inhibitor method is used as a hydrate deposit method. A lot of research is needed. At present, some attempts have been made in this regard to try to find more cost-effective new inhibitors.

(3) How to improve the replacement rate and replacement efficiency and the safety of mining is the difficulty of CO<sub>2</sub> replacement CH<sub>4</sub> hydrate research.

(4) natural gas hydrate collection of various mining methods, whether it is a common method of hydrate mining, or recently proposed new mining methods. Is the technical feasibility of the proposed point of view, the economic feasibility of mining gas hydrate or people plagued a major problem. At this stage, natural gas hydrate has not yet found an economically viable method of mining, still in the research stage. But it is certain that the combination of a variety of principles and methods is the future development trend, will also show attractive prospects.

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