Experimental study on the static formation characteristics of carbon dioxide hydrate

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Abstract: As the most important greenhouse gas affecting the ecological environment, carbon dioxide is converted into oil, and the large-scale use of primary energy such as coal is increasing. The use of hydrate technology to store carbon dioxide on the seabed is an effective way to reduce the carbon dioxide content in the atmosphere. A set of hydrate formation experiment equipment was developed in this paper to simulate the environment of seabed porous media sediments, and CO₂ hydrate was used as the research object to conduct experimental research on hydrate formation characteristics, and to analyze the influence of initial pressure and reaction temperature on the hydrate reaction process. Through a large number of experimental studies, this article mainly obtains the following results: (1) The process of CO₂ hydrate formation is an exothermic reaction. As the initial pressure of the system increases or the reaction temperature decreases, the more heat will be released when hydrate is formed in the kettle, and the peak temperature will naturally be higher. (2) The lower the reaction temperature or the increase in initial pressure, the greater the amount of CO₂ hydrate formation.

1. Introduction

In recent years, the global greenhouse effect and climate change have increasingly severe impacts on human production and life. The emission reduction and treatment of carbon dioxide-based greenhouse gases have attracted widespread attention and attention from domestic and foreign scholars. Using porous media as a carrier to store carbon dioxide gas in the form of hydrates on the seabed is an important way to solve the problem of reducing carbon dioxide gas emissions. Carbon dioxidehydrate is a non-stoichiometric clathrate crystal compound formed by carbon dioxide gas and water under high pressure and low temperature conditions, which can well realize the solidification and storage of carbon dioxide gas. Moreover, the submarine porous media sediment layer has a special environment of low temperature and high pressure, which can continuously increase the formation of carbon dioxide hydrate, so that the permeability and porosity of the submarine sediment layer are drastically reduced, and can block the permeation of carbon dioxide. It is called As the "self-styled process" [1].

There are many studies on natural gas hydrate in porous media in the world. For example, Siangsai et al. [4], Zhang et al. [5], Heeschen et al. [6] conducted methane hydrate formation in activated carbon media, quartz sand, and porous silica gel. Experiments have concluded that media of different particle sizes have a significant impact on the formation kinetics of hydrates. The rate of hydrate formation...
decreases with the increase of the particle size of the media, while the final consumption of methane gas varies with the porous. The pore size of silica gel increases as the pore size increases; Li Shuxia et al. [7] explored the effect of different initial pressure conditions on the formation characteristics of natural gas hydrate in quartz sand, and concluded that the greater the initial pressure, the shorter the induction time for hydrate formation and the amount of hydrate generated will be more; Chen Long et al. [3] studied the formation process and characteristics of natural gas hydrate in different quartz sand media systems under constant volume conditions through experiments, and found that the particle size is 2μm and 5μm. The final water conversion rate and the formation rate of hydrates in the quartz sand media are significantly higher than those of the quartz sand media with a particle size of 229μm. The mass transfer process will affect the formation of natural gas hydrates.

2. Experimental

2.1. Experimental device

Figure 1 is a schematic diagram of a device for conducting experiments on carbon dioxide hydrate formation in natural sea sand. The device consists of six parts: control cabinet, gas supply unit, liquid supply unit, temperature control system, experimental model, and data measurement and transmission unit.

![Diagram of experimental device for static hydrate formation](image)

Fig. 1 Diagram of experimental device for static hydrate formation

- 1-Pressure reducing valve
- 2-Needle valve
- 3-Vent valve
- 4-Gas mass flow meter
- 5-Check valve
- 6-Liquid storage tank
- 7-Constant flow pump
- 8-Gas cylinder
- 9-Pressure gauge
- 10-Differential pressure sensor
- 11-Temperature sensor
- 12-Pressure sensor
- 13-Constant temperature water bath
- 14-Reactor
- 15-Computer
- 16-Collector
The experimental model unit in the system, the reactor, is the core component, which contains an external constant temperature water bath sleeve; under the condition of temperature control in the constant temperature water bath, the liquid supply unit is used to inject liquid into the experimental reactor, and the gas supply unit to stabilize the reactor liquid. Gas can be accurately injected, and the data measurement system can monitor the pressure, temperature and differential pressure changes in the whole process in real time, and then analyze the specific conditions of the CO2 hydrate formation process.

3. Experimental materials
The 99.99% purity of carbon dioxide gas and nitrogen; the secondary deionized distilled water; the natural sea sand was taken from Qingdao offshore and used laser particle size analysis. The analyzer analyzes the particle size and obtains the results shown in Table 1, and the actual product is shown in Figure 2.

| Natural sea sand | Particle size/μm | capacity/% |
|------------------|------------------|------------|
| Clay grade       | <4               | 0.000      |
| Silt grade       | 4~63             | 0.000      |
| Fine sand        | 63~250           | 22.173     |
| Medium sand      | 250~500          | 77.827     |
| Coarse sand      | 500~2000         | 0.000      |
| Gravel           | >2000            | 0.000      |

Fig. 2 The photo of sea sand

(1) After mixing the sand and deionized water evenly, fill it layer by layer into the reactor to form a hydrate deposit layer, connect the pipeline of the entire test system and vacuum; (2) Start the data acquisition instrument and set Good water bath temperature, pour carbon dioxide gas into the kettle to make the pressure in the kettle reach a certain value, check for leaks and let stand for about 24 hours, until the carbon dioxide gas in the natural sea sand is fully dissolved to form a carbon dioxide gas-liquid saturated liquid, record this time Pressure P0 and temperature T0 in the reactor. (3) Cool down the constant temperature water bath to the temperature in the kettle as Tf, and record the pressure Pf in the kettle at this time; when the temperature rises rapidly and the pressure drops rapidly, it indicates that the carbon dioxide hydrate in the reactor starts to be synthesized. (4) After the pressure and temperature of the system are basically stable, indicating that the hydration reaction has been completed and the hydrate formation has ended, record the temperature Ts and pressure Ps at this time. (5) Raise the constant temperature water bath to the initial temperature T0 of the system. After the pressure is stabilized, the carbon dioxide hydrate has been decomposed; keep the system pressure constant, change the reaction temperature Tf in the reactor by adjusting the temperature of the constant temperature water bath, and proceed with different reaction temperatures Experiment on the static formation of carbon dioxide hydrate in natural sea sand. (6) After one round of experiments, discharge
the gas and deionized distilled water in the reactor, and then repeat steps (2) (3) (4) (5) to conduct static carbon dioxide hydrate generation experiments with different pressure and temperature parameters.

4. Experimental study on static formation characteristics of CO₂ hydrate

4.1. Effect of reaction temperature on static formation of CO₂ hydrate

Figure 3 shows the temperature and system pressure changes with time during the hydrate formation process at different reaction temperatures. The initial pressure is 4.5MPa and the initial temperature is 293.9K. Observing Figure 3, it is found that the pressure of the system sometimes rises slightly while the temperature of the system rises rapidly. This is because the gas consumed by the reaction is small at this time and the pressure is greatly affected by temperature changes. In the experiments with reaction temperatures of 270.67K, 271.65K, 272.95K, and 273.57K, the reaction temperature caused by hydrate formation increased by 4.47K, 3.90K, 3.34K, and 2.79K, respectively. It can be seen that the lower the hydration reaction temperature under the same initial conditions, the more heat is released during the reaction. With the decrease of system pressure and the increase of hydrate formation, the rate of pressure decrease in the reactor gradually decreases. After the temperature in the reactor reaches the highest point, it begins to slowly drop and stabilize at the initial set temperature.

According to calculations, in the experiments where the reaction temperature is 270.77K, 271.64K, 272.56K, and 273.50K after the reaction, the stable pressure of the system is 0.98MPa, 1.08MPa, 1.19MPa, 1.23MPa, and the pressure is reduced by 4.08MPa, 3.98 respectively MPa, 3.85MPa, 3.79MPa. It can be seen that the lower the reaction temperature, the lower the stable final pressure in the reactor, and the larger the pressure drop. This is because the equilibrium formation pressure limits the final CO₂ hydrate formation. When the temperature is lower, the pressure for the formation of hydrates is naturally lower, the pressure drop will increase, and the more CO₂ gas will be consumed during the reaction. Then the amount of CO₂ hydrate generated after the reaction is over.

4.2. Effect of initial pressure on static formation of CO₂ hydrate

In this paper, we conducted multiple sets of CO₂ hydrate formation experiments under three different initial pressures. The experimental data related to hydrate formation experiments are listed, including the initial pressure of the system, reaction temperature, induction time, and maximum Parameters such as temperature, temperature increase, stable pressure in the kettle after hydrate synthesis, gas conversion rate, gas consumption, and hydrate storage density.

Figure 4 shows the relationship between system temperature and pressure over time during the hydrate formation process when the initial pressure is 5.0MPa, 4.5MPa and 4.3MPa, and the reaction temperature is 272.6K. The system temperature of the three groups of experiments dropped rapidly to
272.6K and remained stable. As the experiment continued, the temperature in the reactor rose rapidly and then decreased in all three groups of experiments, and finally stabilized at 272.6 At the same time, the pressure in the reactor remained stable after the continuous decrease, and in the experiment with the initial pressure of 5.0MPa, 4.5MPa, and 4.3MPa, the temperature increase in the reactor due to the formation of hydrate could reach 276.87K, respectively. 276.29K, 275.44K, that is, the greater the initial pressure, the higher the peak during the reaction. This is because the greater the pressure of the experimental system, the greater the experimental reaction rate, the more heat released by the reaction, and the greater the maximum temperature reached. The pressure drop amplitudes of the three sets of experiments are also different. It can be seen from the figure that the greater the initial pressure, the greater the corresponding pressure drop and the greater the amount of hydrate formation.

![Fig. 4 Temperature and pressure change vs time (reaction temperature 272.6K)](image)

5. Conclusion
This chapter mainly analyzes and researches the experimental process of natural CO2 hydrate static formation in sea sand. The main conclusions are as follows:

(1) The process of CO2 hydrate formation is an exothermic reaction. As the initial pressure of the system increases or the reaction temperature decreases, the more heat will be released when hydrate is formed in the kettle, and the peak temperature will naturally be higher.

(2) The lower the reaction temperature or the higher the initial pressure, the milder the conditions for the formation of CO2 hydrate and the greater the amount of CO2 hydrate formation.

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