

Experimental Evaluation of Calcium Chloride and Modified Cellulose as Thermodynamic and Kinetic Inhibitors for Natural Gas Hydrate Formation

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ABSTRACT

In deepwater drilling, low-temperature and high-pressure seabed conditions readily promote natural gas hydrate formation, leading to wellbore blockage and operational risks. To mitigate hydrate formation, chemical inhibitors are commonly added to drilling fluids. This study employed an automated visual hydrate reactor under controlled cooling, with real-time monitoring of temperature, pressure, and torque, while methane consumption was quantified using the Peng–Robinson equation. The effects of calcium chloride (CaCl₂, thermodynamic inhibitor) and modified cellulose (CHNF, kinetic inhibitor) were systematically evaluated. Increasing CaCl₂ concentration prolonged nucleation time and reduced nucleation temperature. At 8wt%, the total pressure drop decreased from 5.25MPa (pure water) to 2.46MPa without significant hydrate accumulation; higher concentrations yielded limited additional benefit, and 8wt% was identified as the optimal dosage considering both efficiency and corrosion risk. CHNF displayed a dose-dependent kinetic inhibition effect: at 0.2wt%, the induction time extended to 213 min and nucleation temperature dropped to 8.1°C, whereas 0.1wt% showed negligible effect. Mechanistic analysis suggests that CaCl₂ suppresses hydrate formation by reducing water activity and shifting the gas–liquid equilibrium toward lower temperature and higher pressure, while CHNF delays nucleation and destabilizes hydrate clusters via interfacial adsorption and hydrogen-bond competition. These findings provide practical guidance for optimizing drilling fluid formulations in deepwater operations.

Keywords: natural gas hydrate, drilling fluid, thermodynamic inhibitor, kinetic inhibitor, performance evaluation

NONMENCLATURE

Abbreviations

THIs	thermodynamic hydrate inhibitors
KHIs	kinetic hydrate inhibitors
CHNF	modified cellulose

1. INTRODUCTION

Natural gas hydrate, also known as “combustible ice,” is mainly distributed in permafrost and deep-sea sediments, accounting for over 90% of global reserves. Its decomposition releases large amounts of methane, making it a promising clean energy resource^[1-3]. Developing hydrates efficiently is important for reducing carbon emissions, advancing a low-carbon energy structure, and achieving the “dual carbon” goals. However, low-temperature and high-pressure seabed conditions favor hydrate formation during drilling. Gas intrusion into the wellbore can rapidly trigger hydrate blockages in wellbores and pipelines, hindering operations and causing major economic losses^[4,5]. Thus, systematic investigation of hydrate formation in deepwater drilling fluids and the mechanisms of inhibitors is essential to optimize inhibition performance and ensure wellbore flow and operational safety^[6-9].

Natural gas hydrate formation proceeds in two stages: nucleation, a stochastic molecular process, followed by crystal growth, which leads to the accumulation of stable hydrate structures. Inhibition strategies include dehydration, thermal insulation or heating, depressurization, and the use of chemical additives^[7,10,11]. However, dehydration is applicable only to gas pipelines, insulation and heating are inefficient and costly, and depressurization is impractical during drilling. By contrast, chemical inhibitors are widely adopted owing to their simplicity, cost-effectiveness, and strong inhibitory performance^[12,13].

Hydrate inhibitors are generally divided into thermodynamic hydrate inhibitors (THIs) and kinetic hydrate inhibitors (KHIs)^[4,7,10]. THIs suppress hydrate formation by shifting equilibrium conditions, lowering

the formation temperature and raising the equilibrium pressure^[14-17]. KHIs, typically low-molecular-weight polymers, inhibit nucleation or impede crystal growth through functional groups without altering thermodynamic equilibrium, but instead delay the nucleation time. They are effective at low dosages and exhibit high inhibition efficiency^[18,19]. In this study, the formation behavior of natural gas hydrates and the inhibitory performance of different inhibitor systems were evaluated through experimental research. The effects of the thermodynamic inhibitor calcium chloride (CaCl₂) and the kinetic inhibitor modified cellulose (CHNF) at different concentrations were compared, providing a reference for the efficient application of inhibitors in oilfield operations.

2. MATERIALS AND METHODS

2.1 Experimental materials

The main materials used in this study included methane gas, ultrapure water, calcium chloride (CaCl₂) and modified cellulose (CHNF).

2.2 Experimental apparatus

The fully automated visual hydrate reactor employed in this study is illustrated in Fig.1. The system is composed of a high-pressure reactor vessel, a thermostatic water bath, integrated temperature and pressure sensors, a vacuum pump, and a gas booster system.

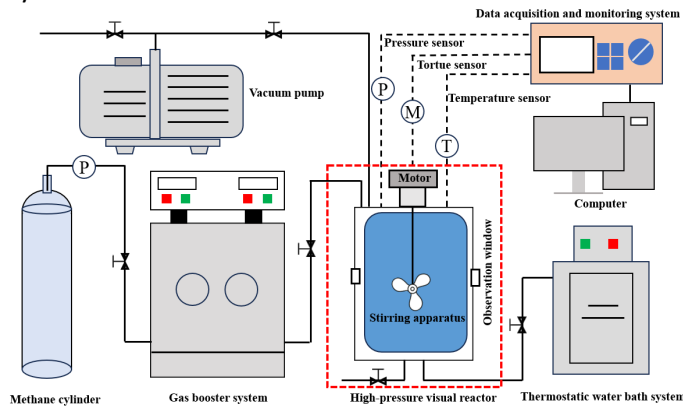


Fig.1 The schematic of the experimental apparatus

2.3 Experimental procedure

In this study, a constant cooling rate was employed, in which the temperature of the high-pressure reactor vessel was programmatically controlled to decrease from 18°C to 0°C. Simultaneously, the temperature control system and the camera capture system were activated, enabling direct observation of gas-liquid changes inside the reactor through the visual window. A data acquisition

system was used to continuously record variations in temperature, pressure, and torque. When the system temperature dropped below the hydrate formation threshold, hydrate nucleation occurred, which could be clearly identified using the visualization apparatus. As hydrate formation is an exothermic process, the temperature and pressure curves exhibited nearly linear trends prior to nucleation. Once hydrate formation began, the release of heat caused a transient increase in system temperature, while the consumption of methane during hydrate growth led to significant pressure reduction. These phenomena were reflected by the appearance of a peak in the temperature curve and a sudden increase in the slope of the pressure curve. The inhibition performance of different additives was then evaluated by comparing the nucleation time, nucleation temperature, and pressure profiles under various inhibitor conditions.

In this study, the methane consumption in the reactor was calculated using the Peng–Robinson equation^[20], which can be expressed as Eq. (1):

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \quad (1)$$

Here, a and b are energy parameters (Pa·m⁶/mol²); P is the system pressure (MPa); T is the temperature (K); R is the gas constant; and V_m is the molar volume (L/mol), which can be calculated using Eq. (2)–(5):

$$a(T) = a(T_c) \alpha(T) = 0.45274 \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (2)$$

$$\alpha(T) = \left[1 + k \left(1 - T_r^{0.5} \right) \right]^2 \quad (3)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (4)$$

$$k = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (5)$$

Here, P_c is the critical pressure (MPa); T_c is the critical temperature (K); T_r is the ratio of the experimental temperature to the critical temperature; and k is a function of the acentric factor ω . Accordingly, the molar consumption of methane is calculated using Eq. (6):

$$\Delta n = \frac{P_1 V_1}{Z_1 T_1 R} - \frac{P_2 V_2}{Z_2 T_2 R} \quad (6)$$

Here, Z is the compressibility factor calculated using the PR equation, where subscripts 1 and 2 denote two points during the formation process.

During the experiments, the liquid volume in the reactor was consistently maintained at 370 mL to ensure that the gas volume involved in each run remained constant. To optimize and standardize the methodology, the stirring speed was set at 400rpm and the cooling rate

at 3°C/h, which were applied in all subsequent experiments.

3. RESULTS AND DISCUSSION

3.1 Blank control experiment

Blank control experiments were conducted with pure water to exclude the influence of impurities and other factors. The typical temperature–pressure profile is shown in Fig.2. As shown in Fig.2, when the reactor temperature gradually decreased to the hydrate formation conditions, the exothermic nature of hydrate generation caused a transient increase in temperature. Meanwhile, the rapid growth and aggregation of hydrate crystals led to a sudden increase in torque. Based on repeated experiments under pure water conditions, the average hydrate nucleation time was approximately 184 min, with a nucleation temperature of 10.2°C. The massive growth stage occurred at about 213 min, corresponding to a temperature of 10.4°C, and the overall pressure drop throughout the process was 5.25 MPa. The corresponding experimental data are summarized in Table 1.

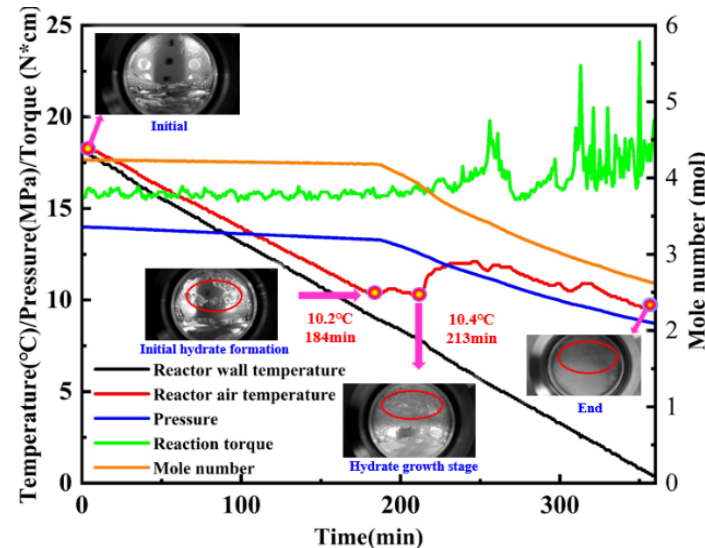


Fig.2 Profiles of hydrate formation in pure water

Table 1 Experimental data of pure water solutions

Solution	nucleation time (min)	nucleation temperature (°C)	Massive growth time(min)	pressure drop (MPa)
pure water	184	10.2	213	5.25

3.2 Performance evaluation of calcium chloride (CaCl₂)

As a thermodynamic hydrate inhibitor, CaCl₂ satisfies the inhibition requirements of most wellbores and pipelines. It offers advantageous physicochemical properties, including high solubility, low viscosity, and shear stability, while being cost-effective, easy to store

and transport, and posing substantially lower risks compared with alcohols and ethers. In addition, its good compatibility with corrosion and scale inhibitors has contributed to its widespread use. In this study, CaCl₂ solutions at concentrations of 3.5wt%, 5wt%, 8wt%, and 10wt% were tested. The corresponding time-dependent profiles of temperature, pressure, torque, and methane consumption were obtained, as illustrated in Fig.3. Analysis of these profiles enabled the determination of hydrate formation onset and quantity, thereby providing a quantitative assessment of the inhibitory performance of CaCl₂ against natural gas hydrate formation.

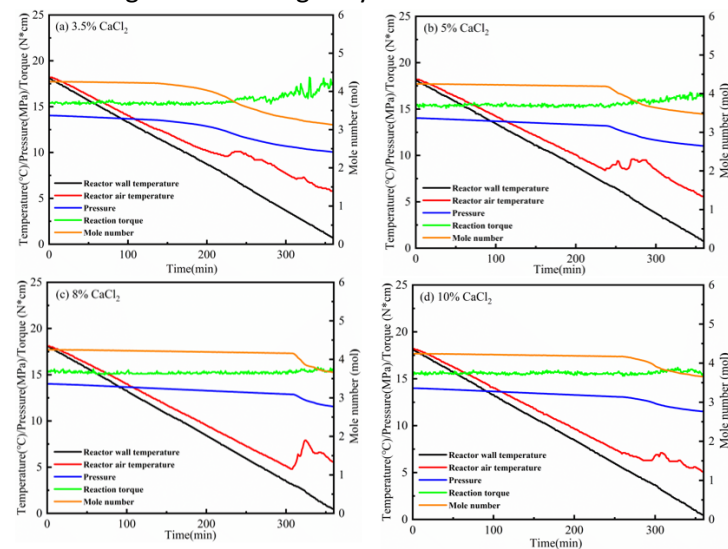


Fig.3 Profiles of hydrate formation under different CaCl₂ concentrations

The inhibitory performance of CaCl₂ solutions at different concentrations was evaluated by analyzing the corresponding profiles shown in Fig.4. For the 3.5wt% solution, hydrate nucleation occurred at approximately 195 min with a nucleation temperature of 10.2 °C; bulk hydrate formation began at around 229 min at 9.6 °C, with a total pressure drop of 3.97 MPa. Although the nucleation time and temperature differed little from those in pure water, the reduced overall pressure consumption indicated a moderate inhibitory effect. With increasing CaCl₂ concentration, inhibition efficiency improved. At 8wt%, the nucleation time was prolonged to about 308 min and the nucleation temperature markedly decreased to 4.8°C. Visual observation revealed no significant hydrate agglomeration, and the total pressure drop declined to 2.46 MPa. These results demonstrate that at 8wt%, CaCl₂ achieves a synergistic effect by substantially delaying nucleation, lowering the nucleation temperature, and reducing gas consumption by nearly half. Increasing the concentration to 10 wt% provided only marginal additional suppression, while elevated Ca²⁺ levels may increase corrosion and scaling

risks. Therefore, 8wt% is identified as the optimal concentration, with 5wt% representing a cost-effective alternative for general application. A summary of the experimental data is provided in Table 2.

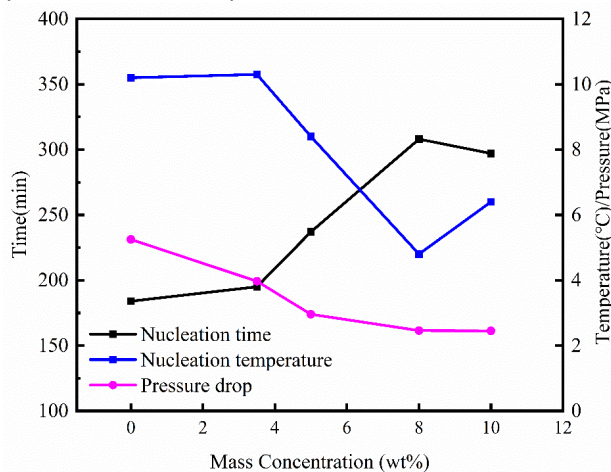


Fig.4 Comparison of nucleation time, temperature and pressure drop of different mass concentrations of CaCl₂

Table 2 Experimental data of CaCl₂ solutions

Solution	nucleation time (min)	nucleation temperature (°C)	Massive growth time(min)	pressure drop (MPa)
pure water	184	10.2	213	5.25
3.5%CaCl ₂	195	10.3	229	3.97
5%CaCl ₂	237	8.4	264	2.96
8%CaCl ₂	308	4.8	Not formed	2.46
10%CaCl ₂	297	6.4	Not formed	2.45

Mechanistic analysis indicates that the inhibitory performance of CaCl₂ is primarily governed by the strong hydration of Ca²⁺ and Cl⁻ ions and the resulting high ionic strength. These effects collectively reduce water activity and shift the hydrate equilibrium toward lower temperatures, requiring colder conditions for nucleation and growth. Ca²⁺, with its high charge density and large hydration number, forms a compact hydration shell that impedes rearrangement of the hydrogen-bonded water network into clathrate cages. The presence of two Cl⁻ ions per Ca²⁺ further elevates ionic strength—nearly three times that of equimolar NaCl—thereby lowering the liquid-phase chemical potential and intensifying the salting-out effect, which reduces methane solubility and effective supersaturation. Additionally, ion hydration increases interfacial tension, viscosity, and mass-transfer resistance, weakening interfacial renewal and diffusion. Collectively, these factors account for the pronounced suppression of hydrate nucleation and growth by CaCl₂.

3.3 Performance evaluation of modified cellulose (CHNF)

Cellulose, as a natural polymer material derived primarily from plants, is environmentally friendly, non-toxic, and biodegradable. When treated with a coupling agent, modified cellulose can serve as a viscosifier and fluid-loss reducer in conventional drilling fluids, while also altering its adsorption capacity to some extent. Considering that hydrate inhibitors typically function by forming hydrogen bonds and adsorbing onto hydrate surfaces, coupling-agent-modified cellulose was employed in this study as a potential hydrate inhibitor, and its performance was evaluated.

In the experiments, the modified cellulose is referred to as CHNF, with concentrations of 0.1wt%, 0.2wt%, 0.5wt%, and 1wt%. Due to limited solubility of the solvent, high-concentration experiments were not feasible; thus, the maximum concentration tested was set at 1wt%. By analyzing the variation curves of temperature, pressure, torque, and molar consumption over time at different concentrations, the inhibitory effect of CHNF on methane hydrate formation was assessed, with the results presented in Fig.5.

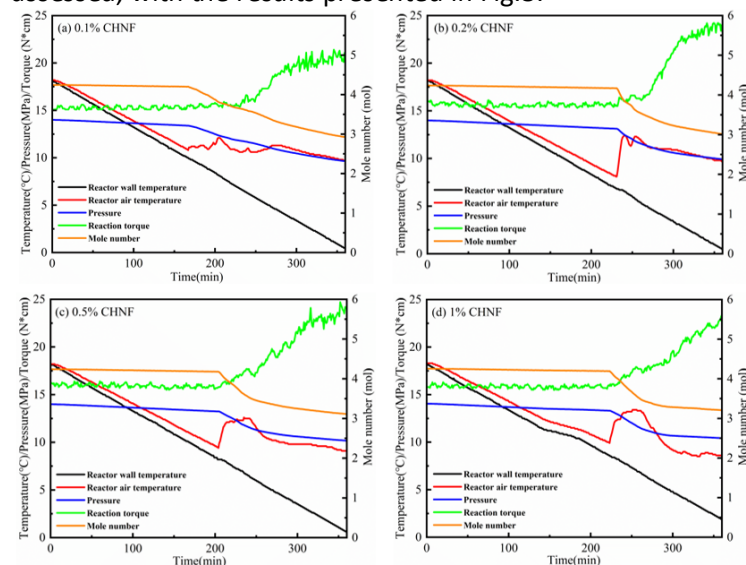


Fig.5 Profiles of hydrate formation under different CHNF concentrations

As shown in Fig.6 and Table 3, the inhibitory performance of CHNF against hydrate formation improved with increasing concentration compared with pure water. The total pressure drop decreased monotonically from 4.37 MPa to 3.62 MPa, indicating continuous suppression of both hydrate quantity and growth rate. At 0.1wt%, nucleation occurred at 167 min, 17 min earlier than in pure water, suggesting negligible inhibition and even slight promotion. In contrast, concentrations of 0.2, 0.5, and 1wt% extended the induction time by 47, 20, and 38 min, respectively, demonstrating enhanced inhibition at higher dosages.

The strongest effect was observed at 0.2wt%, where the induction time reached 231 min and the nucleation temperature decreased to 8.1°C, identifying it as the optimal concentration.

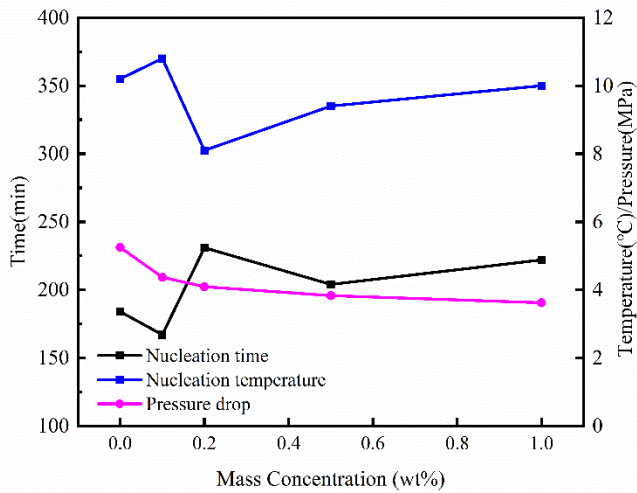


Fig.6 Comparison of nucleation time, temperature and pressure drop of different mass concentrations of CHNF

Table 3 Experimental data of CHNF solutions

Solution	nucleation time (min)	nucleation temperature (°C)	Massive growth time(min)	pressure drop (MPa)
pure water	184	10.2	213	5.25
0.1%CHNF	167	10.8	229	4.37
0.2%CHNF	231	8.1	231	4.09
0.5%CHNF	204	9.4	204	3.83
1%CHNF	222	10	222	3.62

Mechanistically, the modified cellulose functions as a low-dosage, environmentally friendly kinetic inhibitor through a coupled “interface–structure–mass transfer” mechanism, rather than altering thermodynamic equilibrium. The exposed organic functional groups introduced by surface modification preferentially adsorb onto gas–liquid and hydrate crystal interfaces, blocking active sites and increasing the nucleation energy barrier. Meanwhile, –OH groups on the cellulose backbone and polar groups introduced by the coupling agent compete with water for hydrogen bonding, destabilizing hydrate clusters and inhibiting their growth. Additionally, dispersed CHNF forms a weak gel-like viscoelastic network that elevates viscosity, lowers gas diffusivity, and reduces interfacial renewal, thereby further suppressing hydrate development.

4. CONCLUSIONS

(1) Thermodynamic inhibition by CaCl₂: CaCl₂ exhibits a pronounced thermodynamic suppression effect on hydrate formation. Increasing concentration prolongs nucleation time and lowers nucleation temperature;

considering both inhibition efficiency and corrosion risk, 8wt% is identified as the optimal dosage.

(2) Kinetic inhibition by CHNF: Modified cellulose (CHNF) functions as a typical low-dosage kinetic inhibitor. Higher concentrations progressively reduce the overall system pressure drop, with 0.2wt% providing the most effective inhibition.

(3) Mechanistic distinction: CaCl₂ reduces water activity via strong Ca²⁺ hydration and elevated ionic strength, shifting the gas–liquid equilibrium curve toward lower temperatures and higher pressures, thereby limiting hydrate formation. In contrast, CHNF acts by interfacial adsorption and hydrogen-bond competition, which destabilize hydrate clusters, increase molecular resistance, and effectively delay crystal growth.

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