In order to solve the problem of hydrate reservoir collapse and hydrate regenerated in the process of solid fluidization of natural gas hydrate, a new method of natural gas hydrate exploit by high-polymer additive (low viscosity carboxymethyl cellulose LV-CMC) carbon dioxide jet was proposed. The wellbore temperature and pressure changes during this process are analyzed, and the wellbore temperature and pressure model are established and solved by the state space method. This paper also analyzed the effects of relevant parameters on hydrate decomposition, such as injection flow, temperature, and pressure. The results show that increasing the injection pressure allows the hydrate decomposition site to be closer to the annulus outlet. Compared with water, with polymer additive CO₂ fluid as the drilling fluid, the intersection point of phase equilibrium curve and annular pressure curve is closer to annular outlet, which is obviously more conducive to well control. In order to avoid phase changes, the injection pressure of the carbon dioxide fluid of the high-polymer additive should not be lower than 10 MPa, and the injection temperature should not be higher than 285 K.

1. Introduction

Natural gas hydrate has great potential for future energy resources supply, which has the characteristics of wide distribution, shallow burial, and high energy density. According to the conditions of temperature less than 283 K and the pressure greater than 10 MPa, about 27% of the world's land and 90% of the ocean have the potential for gas hydrate formation generation. The reserves of natural gas hydrates in the world are very large. It is estimated that the natural gas resources in hydrates are \(2 \times 10^{16} \text{ m}^3\), which is equivalent to \(2 \times 10^7\) billion tons of oil equivalent, and twice the total amount of carbon of conventional fuels in the world. Traditional gas hydrate mining methods include heat injection method, decompression method, carbon dioxide replacement method, etc. But these methods have not been widely used because of the problems of wellbore safety, production control, and environmental risk [1–3]. The natural gas hydrate solid fluidized mining method could overcome these problems effectively [4]. The method is to use the jet to break the bottom hole hydrate into fine particles, and the hydrate-containing solid particles after fluidization return along the wellbore to the sea surface with the drilling fluid, and finally separate out the natural gas.

In the natural gas hydrate solid fluidized mining method, the hydrate reservoir is liable to collapse, and the decomposed natural gas hydrate may be regenerated, causing blockage of the wellbore and causing a drilling accident [5]. Carbon dioxide fluid containing LV-CMC as jet drilling fluid can effectively solve these problems, on the one hand, because both carbon dioxide and LV-CMC can inhibit the formation of natural gas hydrate; on the other hand, LV-CMC, as a drilling fluid additive, also plays a role in reducing leakage and preventing collapse. In addition, in order to prevent the jet viscosity from being too large and affecting the jet efficiency, we use a jet drilling fluid with an additive concentration of 5%. And when the concentration of the polymer additive is 5%, the physical properties of the carbon dioxide fluid are not greatly affected [6].

Carbon capture and storage (CCS) is a technology that can reduce carbon emissions from fossil fuels on a large scale [7]. The technology was developed in the 1970s for oil, geothermal and other energy development, as well as water treatment and other technologies [8–15]. In the process of extracting natural gas hydrates using high-polymer additive carbon dioxide jet, correct prediction of wellbore temperature and pressure is of great significance for judging the properties of polymer additive CO₂ fluid and analyzing the state of
natural gas hydrate. However, there is very little research work in this field.

Since 1950s, drilling workers have begun to study the temperature distribution of wellbore by numerical simulation and analytical method [15]. The earliest wellbore temperature study was conducted by Ramey, who proposed a steady-state model for obtaining wellbore temperature distribution, which could not be applied to transient behavior [16–19]. Raymond proposed a numerical model for wellbore temperature distribution under pseudo-steady-state conditions [20]. Hansan and Kabir proposed an analytical method for wellbore temperature prediction [21, 22]. For CO2 injection drilling and development methods, wellbore flow and thermal behavior have unique characteristics. Many researchers also developed CO2 two-phase flow models under isothermal conditions [23–24]. However, the process of natural gas hydrate exploitation is different from injecting polymer additive CO2 fluid into wellbore. It also needs to consider the heat transfer of annular, pipeline, seawater, and hydrate decomposition, but this field has not been studied for the time being.

In this paper, the mathematical model of wellbore temperature and pressure during polymer additive CO2 fluid injection is established, and the model is solved by state space method. This method can be used not only to solve partial differential equations, but also as an automatic control model, which lays a foundation for automatic control of temperature and pressure in natural gas hydrate mining process in the future. This study can be used to design the injection parameters of polymer additive CO2 fluid and reduce the risk of using this drilling fluid to extract natural gas hydrate.

2. Materials and Methods

Low viscosity carboxymethyl cellulose (LV-CMC) is a polymer. Hydroxyl OH and ether oxygen group on the macromolecular chain are absorbed to the surface of the hydrate crystal. The polymer forces the hydrate crystal to grow around the polymer with a small radius of curvature, thus reducing the rate of hydrate formation and prolonging the time of hydrate crystal nucleus formation. In view of the fact that fluidized natural gas hydrates may be formed again during deep-water oil and gas drilling, we chose carbon dioxide fluid with LV-CMC as jet drilling fluid.

The change of phase state of CO2 at certain temperature and pressure will lead to change in the properties of carbon dioxide. Figure 1 describes phase change of CO2, when CO2 approaches the supercritical state (31.1°C, 7.38 MPa), which is likely to occur somewhere along the wellbore.

2.1. Thermodynamic Properties. In 1996, Span and Wagne [26] proposed a special equation of state for carbon dioxide (hereinafter referred to as the S-W equation). It can be applied to a wide range of applications (216.59 K < T < 1100 K, 0.52 MPa < p < 800 MPa) with high accuracy. Therefore, it is more suitable to calculate the thermodynamic properties of polymer additive carbon dioxide fluid under high temperature and high pressure.

The S-W equation is expressed in the form of Helmholtz free energy with two independent variable temperatures T and density ρ. The dimensionless Helmholtz free energy Φ(δ, τ) can be divided into the ideal gas part Φδ(δ, τ) and the residual fluid part Φτ(δ, τ), namely:

$$\Phi(\delta, \tau) = \Phi_\delta(\delta, \tau) + \Phi_\tau(\delta, \tau)$$  (1)

Here δ = ρ/ρ_c, τ = T/T_c, dimensionless.

According to the S-W formula and proportion of additive (5%), the solution of the density, isostatic heat capacity, Joule-Thomson coefficient and other thermodynamic properties of the polymer additive CO2 fluid can be obtained.

2.2. Heat Transfer Model. Figure 2 describes the process of injecting the polymer additive CO2 fluid for natural gas hydrate exploitation. The process can be divided into three parts. The first, the polymer additive CO2 fluid is injected into the coiled tubing. The second, the fluids flow through the jet bit and flow into the annulus. The third, the fluids flow through the annulus and to the sea surface.

Based on the principle of conservation of energy, we can establish the dynamic mathematical model of heat transfer in the process of injecting the polymer additive CO2 fluid:

2.2.1. The heat transfer model of tubing fluids. For the polymer additive CO2 fluid in the tubing, the energy change is equal to the heat generated by the axial flow of the fluid, the heat exchange between the fluid in the tubing and the fluid in the annulus, and the heat generated by the pressure change. Therefore, the heat transfer model is:

$$\rho_p A_p C_p \frac{\partial T_p}{\partial t} = -M_p C_p \frac{\partial T_p}{\partial z} + 2\pi r_m \lambda \left[ T_w - T_p \right] + \alpha_p M_p C_p \frac{\partial \rho_p}{\partial z}$$  (2)

Where \( \rho_p \) is the density of tubing fluid, kg/m³, \( A_p \) is the area of the tubing, \( m \), \( T_p \) is the temperature of the fluid in the tubing,
K, $T_a$ is the temperature of the tubing, MPa, $C_p$ is the specific heat of the fluid in the tubing, kg/m$^3$ K$^{-1}$, $r_i$ is the inner radius of tubing, m, $v_i$ is the fluids flow velocity in the tubing, m/s, $\lambda_{12}$ is the convective heat transfer coefficient between tubing and the polymer additive CO$_2$ fluids and tubing, W/m$^2$·K, and $\alpha_p$ is Joule-Thomson coefficient, K/MPa.

2.2.2. Heat transfer model of annulus. According to Figure 2, we can know the heat transfer model of the polymer additive CO$_2$ fluid in the annulus. The energy change is equal to the heat generated by the axial flow of the fluid, the heat transfer between the annulus fluid and the pipeline fluid, and the heat transfer between the wellbore fluid and the annulus fluid. Therefore, the heat transfer model is:

$$
\rho_a A_a C_a \frac{dT_a}{dt} = -M_a C_a \frac{dT_w}{dz} + 2\pi r_2 \Lambda_{21} (T_w - T_a) \\
+ 2\pi r_2 \Lambda_{3} [T_f - T_a] + \alpha_a M_a C_a \frac{dp_a}{dz},
$$

(3)

where $\rho_a$ is the polymer additive CO$_2$ fluid density of annulus, kg/m$^3$, $A_a$ is the area of annulus, m$^2$, $T_w$ is the temperature of the fluid in the annulus, K, $T_a$ is the temperature of the tubing, K, $\rho_a$ is the pressure of the fluid in the annulus, MPa, $C_a$ is the polymer additive CO$_2$ fluid specific heat of annulus fluid, J/kg·K, $M_a$ is the mass flow of injected polymer additive CO$_2$ fluid, kg/s, $r_2$ is the outer radius of tubing, m, $r_1$ is the radius of annulus, m, $\Lambda_{21}$ is the convection heat transfer coefficient of annular fluid and tubing, $\Lambda_3$ is the convection heat transfer coefficient of annular fluid and borehole wall, W/m$^2$·K,$\alpha_a$ is the Joule-Thomson coefficient, K/MPa.

2.2.3. Heat transfer model of tubing. For the tubing, the change of energy is equal to the convection heat transfer between the annulus fluids and tubing, and the convection heat transfer between the tubing fluids and tubing. Therefore, the heat transfer model is:

$$
\rho_a A_a C_a \frac{dT_w}{dt} = 2\pi r_2 \Lambda_{21} [T_a - T_w] + 2\pi r_1 \Lambda_{12} [T_p - T_w],
$$

(4)

where $\rho_a$ is the density of tubing, kg/m$^3$, $A_a$ is the area of tubing, m$^2$, and $C_a$ is the specific heat of tubing, J/kg·K.

2.3. Wellbore Pressure Model. According to the mass conservation equation and momentum equation, we can get the wellbore pressure model:

$$
\frac{\partial}{\partial z} [p_a v_a^2] = -\frac{\partial p_a}{\partial z} + \rho_a g \sin \theta - f \rho_a v_a^2 \frac{\partial}{\partial z},
$$

(5)

where $f$ is Darcy friction factor and $v_a$ is annulus flow rate, m/s.

2.4. Hydrates Phase Equilibrium Model. According to Dzyuba’s natural gas hydrate phase equilibrium model [4], the relationship between temperature and pressure is:

$$
p_E = \frac{T_a - 264.9661}{9.6339},
$$

(8)

where $p_E$ is hydrate phase equilibrium pressure at the temperature $T_a$, MPa.

2.5. State-Space Method for the Wellbore. For Equation (4), using difference instead of integral, therefore:

$$
\frac{\partial T}{\partial t} = \frac{T(k+1,1) - T(k,1)}{\Delta t},
$$

$$
\frac{\partial T}{\partial z} = \frac{T(1,j) - T(1,j-1)}{\Delta z},
$$

(9)

Equation (2) can be expressed as:

$$
\rho_a A_a C_a \frac{T_a(k+1,j) - T_a(k,j)}{\Delta t} = -M_a C_a \frac{T(k+1,j) - T(k,j)}{\Delta z} \\
+ 2\pi r_2 \Lambda_{21} [T_a(k,j) - T_a(k,j-1)]
+ 2\pi r_2 \Lambda_{3} [T_f(k,j) - T_a(k,j)]
+ \alpha_a M_a \frac{\partial p_a}{\partial z}.
$$

(10)

The depth of wellbore is divided into L nodes, according to linear system theory, each grid temperature in the tubing and annulus is a state. We set the gas injection temperature as $T_i(0)$, and set $x_1 = -(M_a \Delta t)/(\rho_a A_a \Delta z)$, $x_2 = 2\pi r_2 A_2 \Delta t/(\rho_a A_a C_a)$, $x_3 = 2\pi r_2 \Lambda_{3} \Delta t/(\rho_a A_a C_a)$, $Q = \alpha_a M_a \frac{\partial p_a}{\partial z}$, the state-space model for wellbore heat transfer system can be represented as:
\[ T_A(k + 1) = A_a T_A(k) + B_a T_w(k) + C_a T_f(k) + D_a U_a(k), \]  
where,

\[ T_A(k) = \begin{bmatrix} T_A(k, 1), T_A(k, 2), \ldots, T_A(k, L) \end{bmatrix}^T \]  
\[ T_w(k) = \begin{bmatrix} T_w(k, 1), T_w(k, 2), \ldots, T_w(k, L) \end{bmatrix}^T \]  
\[ T_f(k) = \begin{bmatrix} T_f(k, 1), T_f(k, 2), \ldots, T_f(k, L) \end{bmatrix}^T \]

\[ U_a(k) = \begin{bmatrix} T_A(k, 0), Q, 0, \ldots, 0 \end{bmatrix}^T \]

\[ A_a = \begin{bmatrix} x_1 + 1 - x_2 - x_3 & 0 & 0 & \cdots & 0 \\ -x_1 & x_1 + 1 - x_2 - x_3 & 0 & \cdots & 0 \\ 0 & -x_1 & \ddots & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & \ddots \end{bmatrix}, \]

\[ B_a = y_2, \quad C_a = x_3, \quad D_a = -x_1, \]

\[ T_A \] is the state vector of wellbore heat transfer state-space model, \( U_a \) is the input vector, and \( A_a \) is the system matrix. In the same way, we can get the state space model of the fluid temperature in the tubing.

\[ T_p(k + 1) = A_p T_p(k) + B_p T_w(k) + D_p U_p(k). \]  

In this process, the heat sources are the seawater temperature, the formation temperature and the hydrate reservoir temperature, according to literature [4], we can calculate the seawater temperature

\[ T_s = \frac{1}{200} \left[ (T_{s0} - 273.15)(200 - z) + 13.7h \right], \quad 0 \leq z < 200 \text{ m} \]

\[ T_s = a_1 - \frac{a_4 - a_2}{1 + e^{z/a_3/a_4}}, \quad z \geq 200 \text{ m}, \]  

where \( T_s \) represents the temperature of seawater, \( K \); \( T_{s0} \) represents the temperature of sea surface, \( K \); \( z \) represents the depth of seawater, \( m \); \( a_1, a_2, a_3, a_4 \) represent curve fitting coefficients, respectively.

### 3. Results

In order to verify this model, we do simulation to get the distribution of wellbore temperature and pressure and the location of gas hydrate decomposition point under different conditions. The basic data of the simulation derived from literature [4, 23], and are shown in Table 1.

#### 3.1. The Influence of Injection Rate

When the injection rates of the polymer additive CO_2 fluid are 40 L/min, 60 L/min, 80 L/min, and 100 L/min, using this model, the annulus temperature and pressure can be obtained.

Figure 3 shows the temperature distribution of annulus under different polymer additive CO_2 fluid injection rates. The larger the drilling fluid flow rate, the shorter the heat exchange time between the annulus and the seawater, and the less the temperature of annulus is affected by seawater.

Figure 4 shows that annulus pressure decreases as the flow rate increases. For the upper section of wellbore, the phase equilibrium pressure decreases as the flow rate increases, for the lower section of wellbore, the phase equilibrium pressure changes almost unchanged with the change of flow rate. The intersection of annulus pressure and phase equilibrium pressure curve moves upward (The intersection point refers to the critical decomposition position of the natural gas hydrate); this is contrary to the conclusion in [4]. Under this condition of injection temperature and pressure, the decomposition position of hydrate is between depth 150 and 200 m.

During the actual drilling process, phase changes of the polymer additive CO_2 fluid are not expected. According to Figures 4 and 5, the minimum pressure and maximum temperature of the polymer additive CO_2 fluid are at the annulus outlet. The temperature and the pressure corresponding to the different flow rates are shown in Table 2. According to the S-W equation, there is no phase change during this process. In practice, in order to ensure operation safely, the injection pressure should be increased and the injection temperature should be reduced as possible.

#### 3.2. The Influence of Injection Temperature

Figure 5 shows the annulus pressure and phase equilibrium curves under different temperatures, when the flow rate is 100 L/min. Due to the injection temperature increase, the phase equilibrium pressure increases, and the annulus pressure increases a little. The injection temperature effects on the depth of decomposition point very little.
3.3. Comparison With Water. In order to compare the difference between using polymer additive CO₂ fluid and using water as drilling fluid, we do the simulation. As in practice, water is difficult to achieve low temperature as a drilling fluid, the injection water temperature is set at 285 K, the injection pressure is 10 MPa, and the injection amount is 10 L/min. The polymer additive CO₂ fluid injection temperature is 275 K, and other conditions keep the same.

Figure 6 shows the annulus temperature distribution. Since the specific heat of the polymer additive CO₂ fluid is less than the specific heat of the water, it is greatly affected by the seawater...
temperature. Figure 7 shows the relationship between the annulus pressure and the phase equilibrium pressure. The equilibrium curves of the two are almost coincident. When polymer additive CO$_2$ fluid is used as the drilling fluid, the decomposition position of the hydrate is closer to the wellhead.

4. Conclusions

Based on the above study, we can draw the following conclusions:

1. Increasing the pressure of injection can get the hydrate decomposition position closer to the annulus outlet.
2. Compared with water, using polymer additive CO$_2$ fluids as drilling fluids, the intersection of phase equilibrium curve and the annulus pressure curve is closer to the annulus outlet, which is obviously beneficial to the implementation of well control.
3. However, due to the special properties of the polymer additive CO$_2$ fluid, in order to ensure that the polymer additive CO$_2$ fluids do not result in a phase change during the drilling process, it is necessary to increase the pressure and reduce the temperature of the injection CO$_2$; this is very difficult for the equipment. According to the calculation, it is suggested that the injection pressure should not be lower than 10 MPa and the injection temperature should not be higher than 285 K.
4. When the polymer additive CO$_2$ fluid is used as the drilling fluid, the intersection of the phase equilibrium curve and the annulus pressure curve increases as flow rate increases, which is contrary to the conclusion in [4]. The reason is the focus of future research.

**Data Availability**

All data included in this study are available upon request by contact with the corresponding author.

**Conflicts of Interest**

The authors declare that there is no conflict of interest regarding the publication of this paper.

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