A New Model of Displacement Efficiency of Gas Hydrate Considering the Influence of Temperature

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Abstract: The model of natural gas hydrate displacement failed to accurately analyze the influence degree of temperature, and it is not accurate enough to calculate the volume of gas under high pressure owing to the influence of compressibility factor, which leading to a result that the model has great error in calculating the displacement efficiency. In this paper, a new model of displacement efficiency affected by temperature is derived in the design of displacement experiment based on the law of conservation of mass, Multicomponent gas equation of state, Multicomponent thermodynamic phase equilibrium principle at the first. Next, several methods for calculating the compressibility factor of natural gas at different temperatures and pressures are compared by using Visual Basic software, and the Setzmann equation with the smallest error is selected. Finally, compared with the new model, the traditional model as well as the experimental data, the results show that the new model is closer to the experimental data. At the same time, the displacement efficiency of natural gas hydrate at different temperatures is analyzed. It is suggested that higher displacement efficiency can be obtained by reasonably increasing the temperature of the displacement reaction system.

1. Introduction

At present, the research on gas hydrate exploitation method at home and abroad is at the stage of theoretical demonstration and experimental simulation. The research methods mainly include: Displacement mining method [1]; Ground decomposition method [2], Injection inhibitor method [3], Reduction of pressure mining method [4], Thermodynamic method [5]. In the process of the Surface Decomposition, because of the continuous excavation of shallow seabed geology, it will to a great extent cause serious geological hazard to the undersea shallow loose formation [6]; the formation pollution is apt to be caused by traditional thermodynamic inhibitors in the process of injecting inhibitors. However, the main purpose of the new kinetic inhibitors is to prevent the secondary formation of hydrates during the pipeline transportation of natural gas[7]; During the process of depressurization, the percolation capacity of the reservoir will decrease quickly, which would result in the porosity of the hydrate reservoir being compressed and the degree of development is low[8]; Usually, the Thermodynamic method is used in the case of low thermal conductivity, and the energy loss is large during the mining process [9]. The method using carbon dioxide to replace methane gas dissolved in hydrate can not only make rational and effective use of carbon dioxide emitted by industry, but also can develop natural gas hydrate efficiently. In recent years, the research on the efficiency of displacement has become a hot spot in hydrate development field.

The experimental results show that the cage structure of natural gas hydrate will not be destroyed and reorganized in the process of gas hydrate extraction by carbon dioxide displacement, that is, the natural gas hydrate will not decompose. The displacement process would take place in situ, and the hardness will not be reduced, so there will be no signal of formation instability, which shows that the prospect of application is well. Because of the constraints of current technical conditions, the displacement technology
of carbon dioxide has the problem of low replacement efficiency. In this paper, a new model of displacement efficiency affected by temperature is proposed, which can improve the degree of displacement reaction by adjusting the temperature of displacement system reasonably.

2. New displacement model of considering temperature

According to the relationship between the decomposition amount of methane hydrate at different displacement temperature and time under the condition of experiment, Li Z.Z. pointed out that the higher temperature can promote the reaction of displacement [10]. Wang J.B measured the methane production at two different temperatures by gas chromatograph under the condition of isobaric pressure. The experimental results show that the ratio of methane in the gas component increases as the temperature increases, indicating that the degree of displacement increases with the increase of temperature [11]. In the course of studying thermodynamics in displacement reaction, Yang G [12] pointed out that the thermal stability of carbon dioxide hydrate is better than that of methane hydrate, and suggested that the rising temperature can increase the displacement efficiency in a certain temperature range. Wang X.W pointed out that carbon dioxide gas and free water in sediment can form carbon dioxide hydrate during displacement process, leading to a result that the displacement efficiency is lower than the actual value [13]. Qi Y.X defines the displacement efficiency as the mole fraction of methane in the sample gas, and points out that the displacement efficiency would be increasing with the increase of temperature [14]. Sun J.Y pointed out that the temperature had little effect on the displacement efficiency in the rapid displacement stage in the displacement experiment; however, it would increase obviously with the increase of temperature in the slow reaction stage [15].

2.1 The synthesis stage of natural gas

In this paper, the displacement efficiency is defined as the ratio of the amount of methane replaced by carbon dioxide to the amount of methane involved in the synthesis. In order to avoid the inaccuracy of displacement efficiency caused by the reaction of carbon dioxide gas with in situ free water to form carbon dioxide hydrate, the model in this paper focuses on the effect of temperature on hydrate synthesis and displacement. A large number of carbon dioxide gases are allowed to be stored under the condition that methane gas displacement is guaranteed.

Under the experimental conditions, the synthesis of methane hydrate occurred in the sand filling pipe. The methane phase is taken as a few phase, as the default synthesis is SI hydrate and the hydrate is incompressible. The pore volume of filling sand is V, the pre-pressure of hydrate synthesis is P1, the pressure of T1, the post-synthesis pressure of hydrate is P2 and the temperature is T2. According to the principle of isovolumetric synthesis. The equation traditional model is as equation (1). On this basis, according to the law of conservation of mass [16]. The equation model taking the effect of temperature on volume into the consideration is as equation (2)

\[
V_{w1} + V_{G1} = V_{G2} + V_{w1} + V_{w2}
\]

\[
V_{w1}\rho_{w1} + \frac{0.1T_1}{273.15P_1}\rho_{G1} = \frac{0.1T_2}{273.15P_2}\rho_{G2} + V_{h1}\rho_{h1} + V_{w2}\rho_{w2}
\]

In the equation:

\(V_{w1}\): is the initial water injection volume of the reaction and it can be measured by the advection pump, cm³;

\(V_{w2}\): is the volume of residual water phase after reaction, cm³;

\(V_{G1}\): is the volume of the methane under the initial standard condition, cm³;

\(V_{G2}\): is the volume of the residual methane gas after the reaction, cm³;

\(V_{h1}\): is the volume of the hydrate formed by the reaction, cm³;

\(\rho_{w1}\): is the density of water injected before reaction, g/cm³;

\(\rho_{G1}\): is the density of methane before reaction, g/cm³;

\(\rho_{G2}\): is the density of methane at the end of the reaction, g/cm³;

\(\rho_{w2}\): is the density of water injected at the end of the reaction, g/cm³;
\( \rho_{h1} \): is the density of Natural Gas Hydrate after reaction, g/cm\(^3\);

The hypothesis of the experiment includes:

1. Methane dissolved in aqueous solution does not increase the volume of water;
2. The ratio of SI type gas hydrate to gas is 1: 168, and the proportion of water is 1: 0.8;
3. In the synthesis process, methane gas completely occupies the small cage and cage structure of hydrate.
4. In the process of synthesizing natural gas hydrate from methane and water, the mass before and after the system does not change.

The above formula is transformed to:

\[
V_{w1} = \frac{V_{g1} - V_{g2} - V_m}{168} 
\]  
\[
V_{w2} = V_{w1} - 0.8 \frac{V_{g1} - V_{g2} - V_m}{168} 
\]

In the equation:

- \( Z_1 \): is the compression factor of methane gas at the initial reaction temperature and pressure, dimensionless;
- \( Z_2 \): is the compressing factor of methane gas after the end of the reaction, dimensionless;
- \( V_m \): is the volume of methane gas dissolved in water, cm\(^3\);

The solubility of gases in liquids can be calculated by Henry's Law:

\[
[X(\text{aq})] = K_H P_H 
\]

The equation above shows that more methane gas can be involved in the synthesis process when the temperature \( T_1 \) of reaction in hydrate synthesis system is lower, which can lead to more natural gas hydrate.

2.2 The displacement process of natural gas

In the process of displacement, carbon dioxide molecules can only replace methane molecules in the cage structure of hydrate. The hypothesis of the displacement includes:

1. The volume of carbon dioxide injected is \( V_{G3} \);
2. The initial temperature of displacement reaction is \( T_3 \);
3. During the displacement, the pressure of the reaction system is controlled by the injection of carbon dioxide. The injection pressure of carbon dioxide gas is assumed to be \( P_3 \). The equation of state has the following equation:

\[
T_2 = T_3 
\]

\[
Z_2 = \frac{Z_2}{P_2 V_{G2}} = \frac{Z_2}{P_3 V_{G3}} 
\]

In the equation:

- \( Z_2 \): is the compressibility factor of carbon dioxide gas at the beginning of displacement reaction, dimensionless, cm\(^3\)/cm\(^3\);
- \( V_{G3} \): is the volume of carbon dioxide injected under standard conditions, cm\(^3\);
- \( P_3 \): is the pressure of the system obtained:
The displacement pressure can be changed by changing the volume of carbon dioxide injected. The initial temperature of displacement reaction is set as \( T_3 \), and the temperature of displacement reaction system is kept constant by constant temperature equipment. The reaction is complete when the pressure of the reaction system remains stable for 10 minutes. At this point, the pressure remains \( P_4 \). Since both methane and carbon dioxide molecules can form SI hydrates with water, it is assumed that the hydrate phase does not change in volume during the displacement reaction but changes in compression factors due to pressure changes. According to the principle of volume invariance of the reaction system, the equation traditional model is as equation (11). On this basis, according to the law of conservation of mass. The equation model taking the effect of temperature on volume into the consideration is as equation (12):

\[
\begin{align*}
V_{G4} + V_{G5} &= V_{G4} + V_{G5} + V_{w3} + V_{w3} \\
V_{G4} \rho_{G4} + V_{G5} \rho_{G5} &= V_{G4} \rho_{G4} + V_{G5} \rho_{G5} + V_{w2} \rho_{w2} + V_{w3} \rho_{w3}
\end{align*}
\]

(11)  
(12)  

\[
\begin{align*}
V_{G4} &= \frac{\Delta V}{168} \\
V_{G5} &= \frac{0.12 T_3}{273.15 P_3} \\
V_{G5} &= \frac{0.12 Z_3}{273.15 P_4} \\
V_{w2} &= V_{G4} - V_{G5} \\
V_{w3} &= 0.8 V_{w2}
\end{align*}
\]

(13)  
(14)  
(15)  
(16)  
(17)

In the equation:  
\( V_{G4} \): is the volume of methane at the end of displacement, cm\(^3\);  
\( V_{G5} \): is the volume of carbon dioxide at the end of displacement, cm\(^3\);  
\( \rho_{G4} \): is the density of methane at the end of displacement, g/cm\(^3\);  
\( \rho_{G5} \): is the density of carbon dioxide at the end of displacement, g/cm\(^3\);  
\( \rho_{w2} \): is the density of natural gas hydrate at the end of displacement, g/cm\(^3\);  
\( V_{w3} \): is the volume of water at the end of displacement, cm\(^3\);  
\( \rho_{w3} \): is the density of water at the end of displacement, cm\(^3\);  

When the process of displacement have finished, the amount of gas solution can be obtained according to the principle of equal chemical potential of gas and liquid in the displacement system. There is no methane incorporation in the gas component at the end the displacement reaction. The displacement efficiency \( \eta \) can be defined as the ratio of the amount of methane gas \( V_{G4} \) replaced to the quantity \( \Delta V \) involved in the synthesis of methane gas. The \( \eta \) can be obtained by combining with the upper equation.

\[
\eta = \frac{V_{G4}}{\Delta V}
\]

(18)

3. Error analysis of multicomponent equation of state model

It is necessary to determine the gas phase density of methane when calculating the displacement efficiency. Generally, the compressibility factor of methane can be calculated by the state equation; however, the compressibility factor calculated by the different state equation is quite different. The small deviation of the compressibility factor will lead to large experimental error while hydrate synthesis and displacement due to pressure variation. The empirical formula is calculated by Visual Basic and the compressibility factor of methane is calculated at certain temperature 303.15K, 373.15K and pressure from 2.5 to 32.5MPa, including Setzmann equation; Soave RK equation; RK equation; PR equation.

As shown in figure 1-Table2, the compressibility factor calculated by the Setzmann equation is almost equal to that in the NIST database. However, taking the compression factor of methane in the database of NIST (the standard of national institute and technology) as a reference, the other formulas have big deviations when the pressure goes up to 5MPa. The error of the results calculated for each equation is shown in Table 3-Table 4.
The formulas of calculating the compressibility factor of gas[19-22]:

Setzmann equation:

$$ \frac{p(\delta, \tau)}{\rho RT} = 1 + \delta \frac{e}{\delta \rho} \frac{\delta e}{\delta \tau}, \delta = \frac{P - \rho_e e}{\rho_e}, \tau = \frac{e}{T} $$  \hspace{1cm} (19)$$

SRK equation:

$$ P = \frac{RT}{V_n - b} - \frac{a(T)}{V_n (V_n + b)}, a = 0.42748 \frac{R^2 T_e^2}{P_e}, b = 0.08664 \frac{RT}{P_e} $$  \hspace{1cm} (20)$$

RK equation:

$$ P = \frac{RT}{V_n - b} - \frac{aT^{-0.5}}{V_n (V_n + b)}, a = 0.42748 \frac{R^2 T_e^{2.5}}{P_e}, b = 0.08664 \frac{RT}{P_e} $$  \hspace{1cm} (21)$$

PR equation:

$$ P = \frac{RT}{V_n - b} - \frac{a(T)}{V_n (V_n + b) + b(V_n - b)}, a = 0.45724 \frac{R^2 T_e^2}{P_e}, b = 0.07780 \frac{RT}{P_e} $$  \hspace{1cm} (22)$$

Table 1: Compressibility factors of each equation at 305.15K.

| Pressure (MPa) | PR    | NIST   | Setzmann | RK    | SRK    |
|---------------|-------|--------|----------|-------|--------|
| 2.5           | 0.95  | 0.96   | 0.92     | 0.96  | 0.96   |
| 5             | 0.9   | 0.92   | 0.89     | 0.92  | 0.92   |
| 7.5           | 0.87  | 0.86   | 0.84     | 0.86  | 0.86   |
| 10            | 0.82  | 0.84   | 0.83     | 0.84  | 0.84   |
| 12.5          | 0.81  | 0.83   | 0.83     | 0.85  | 0.85   |
| 15            | 0.81  | 0.83   | 0.85     | 0.87  | 0.89   |
| 17.5          | 0.81  | 0.85   | 0.87     | 0.89  | 0.91   |
| 20            | 0.81  | 0.87   | 0.89     | 0.91  | 0.94   |
| 22.5          | 0.81  | 0.89   | 0.93     | 0.94  | 0.96   |
| 25            | 0.81  | 0.89   | 0.96     | 0.96  | 0.97   |
| 27.5          | 0.81  | 0.89   | 0.96     | 0.96  | 0.98   |

Table 2: Compressibility factors of each equation at 375.05K.

| Pressure (MPa) | PR    | NIST   | Setzmann | RK    | SRK    |
|---------------|-------|--------|----------|-------|--------|
| 2.5           | 0.98  | 0.98   | 0.97     | 0.98  | 0.97   |
| 5.00          | 0.96  | 0.97   | 0.96     | 0.97  | 0.97   |
| 7.50          | 0.94  | 0.95   | 0.94     | 0.96  | 0.97   |
| 10            | 0.93  | 0.95   | 0.94     | 0.96  | 0.98   |
| 12.5          | 0.93  | 0.96   | 0.94     | 0.96  | 0.98   |
| 15            | 0.93  | 0.96   | 0.94     | 0.96  | 0.98   |
| 17.5          | 0.93  | 0.96   | 0.95     | 0.96  | 0.98   |
| 20            | 0.93  | 0.96   | 0.96     | 0.96  | 0.99   |
| 22.5          | 0.93  | 0.96   | 0.96     | 0.97  | 0.99   |
| 25            | 0.93  | 0.96   | 0.96     | 0.97  | 0.99   |
| 27.5          | 0.93  | 0.96   | 0.96     | 0.97  | 0.99   |

Table 3: Relative errors of each equation at 305.15K.

| Pressure (MPa) | PR      | Setzmann | RK      | SRK     |
|---------------|---------|----------|---------|---------|
| 2.5           | -1.12   | -0.01    | -0.24   | 0.12    |
| 5.00          | -1.91   | -0.01    | -0.31   | 0.48    |
| 7.50          | -2.40   | -0.01    | -0.24   | 1.01    |
| 10            | -2.50   | -0.01    | 0.03    | 1.73    |
| 12.5          | -2.43   | 0.00     | 0.45    | 2.55    |
| 15            | -2.23   | 0.00     | 0.95    | 3.31    |
| 17.5          | -2.07   | 0.00     | 1.44    | 3.93    |
| 20            | -2.10   | 0.00     | 1.74    | 4.30    |
| 22.5          | -2.26   | 0.00     | 1.91    | 4.43    |
| 25            | -2.62   | 0.01     | 1.94    | 4.40    |
| 27.5          | -3.01   | 0.01     | 1.88    | 4.24    |
30.0  -3.46  0.01  1.75  3.95
32.5  -3.95  0.01  1.56  3.62

Table.4 Relative errors of each equation at 375.05K.

| Pressure (MPa) | PR  | Setzmann | RK  | SRK  |
|---------------|-----|----------|-----|------|
| 2.50          | -0.74 | -0.02   | -0.25 | 0.25 |
| 5.00          | -1.23 | -0.02   | -0.38 | 0.54 |
| 7.50          | -1.62 | -0.02   | -0.44 | 0.93 |
| 10.0          | -1.89 | -0.02   | -0.48 | 1.33 |
| 12.5          | -2.05 | -0.02   | -0.48 | 1.75 |
| 15.0          | -2.11 | -0.02   | -0.41 | 2.15 |
| 17.5          | -2.18 | -0.02   | -0.34 | 2.48 |
| 20.0          | -2.28 | -0.02   | -0.25 | 2.74 |
| 22.5          | -2.38 | -0.02   | -0.18 | 2.97 |
| 25.0          | -2.54 | -0.02   | -0.11 | 3.10 |
| 27.5          | -2.70 | -0.02   | -0.08 | 3.13 |
| 30.0          | -2.93 | -0.02   | -0.08 | 3.10 |
| 32.5          | -3.20 | -0.02   | -0.15 | 3.03 |

From the Table above, we can see that the error of between the results calculated by Setzmann equation and compression factor in NIST database is the least. The relative errors calculated by other empirical formulas are relatively large. Among them, the competition equation of PK is the least error. The errors of result calculated by PRSV1 and PRSV2 equations are almost equal, but they are more larger comparing with the competition equation of PK. The order of relative error from large to small can be gotten as: ESD equation, SRK equation, PRSV equation, PR equation and Vanderwaals equation. According to the Table above, the relative error decreases with the increase of temperature of reaction.

According to equation (18), the efficiency of displacement can be influenced by the value of P/Z directly. Therefore, the error of P/Z obtained from different equations of state is calculated by using the compressibility factor calculated from the NIST database regarded as the standard reference (Table. 5). The error between NIST and P/Z calculated by Setzmann equation is close to zero, which can be ignored. The trend of P/Z calculated by R-K equation, S-R-K equation and P-R equation is basically the same. And the characteristics of them can be described as “increase firstly, then decline, and rise slowly”. The P/Z calculated by P-R equation is always larger, so the efficiency of displacement is higher. The P/Z calculated by S-R-K equation is always small, so the efficiency of displacement is small. The P/Z calculated by R-K equation is larger firstly and then smaller, so the efficiency of displacement is larger first and then smaller. The difference between R-K equation and Setzmann equation is very small when the pressure is lower than 4MPa. So, the Setzmann equation with minimum error is chosen when calculating the compressibility factor of gas.

Table.5 P/Z errors of each equation at 305.15K.

| Pressure (MPa) | SRK  | RK  | Setzmann | PR   |
|---------------|------|-----|----------|------|
| 0.0928        | -0.0220 | -0.0220 | -0.0220 | -0.0220 |
| 2.5066        | -0.1542 | 0.1542  | -0.0220 | 1.0793  |
| 5.0133        | -0.5066 | 0.2863  | -0.0220 | 1.9163  |
| 7.5199        | -1.0352 | 0.1982  | -0.0220 | 2.4449  |
| 10.0265       | -1.7401 | -0.0220 | -0.0220 | 2.5771  |
The Setzmann equation of state is usually used to calculate the compressibility factor of natural gas hydrate in the synthesis of hydrate and in replacement process [17,23]. Table above display, the error between the compression factor calculated by the formula and the NIST database is least in the range of hydrate synthesis pressure. In this paper, the accuracy of the traditional model and the improved new model are compared and analyzed in the process of natural gas synthesis and the displacement of carbon dioxide.

4.1 The synthesis stage of natural gas
Li X.G analyzed the variation of gas holdup with time at temperature 0.9°C, 4.0°C, 5.2°C and 7.0°C, respectively. The experimental data showed that the rate of gas hydrate rising was faster when the temperature of the system was lower. In Li X.G’s experiment, the initial water volume of injection, \( V_{w1} = 150\text{mL} \); pore volume, \( V = 2050\text{cm}^3 \); the initial pressure, \( P_1 = 5.8\text{MPa} \) [24]. Define the ratio of methane volume as the ratio of methane volume \( \Delta V \) to hydrate volume participating in the reaction under standard conditions. According to formula (9), the volume of methane in the modified model and the volume gas holdup of the model can be obtained. Finally, the traditional hydrate model, the new model and the experimental data of Li X.G are compared. Under the temperature and pressure given by the experimental conditions, the volume gas holdup at different times can be calculated. At the same time, the relationship between the volume gas holdup of pre 200min and time is plotted, as shown in Table 6.

By analyzing the data above, the gas holdup of the two models is basically the same in the initial stage of the synthesis reaction that is called the induced synthesis stage. This may be caused by the fact that only a small amount of methane molecules were dissolved in the solution of the system in the early stages of hydrate formation, overcoming the surface tension. The ratio of gas holdup is low and the difference between the two equations is small. With the development of the reaction, the ratio of gas holdup increases rapidly in the later stage of hydrate synthesis. At this point, with the change of the pressure of the system, the error caused by the traditional model increases because the influence of temperature is not taken into account, which leads to the larger error between the volume gas content and the measured data. However, the new model is close to the experimental data of Li X.G, as shown in Table 6 [20-25].

Table 6 Comparative diagram of volume gas holdup calculated by new model and measured gas holdup.

| Time (min) | 10.00 | 20.00 | 40.00 | 60.00 | 80.00 | 100.0 | 120.0 | 140.0 | 160.0 |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Experiment (%) | 9.00  | 43.78 | 104.3 | 132.6 | 144.1 | 146.7 | 147.5 | 148.3 | 149.1 |
| Traditional model (%) | 9.00  | 46.78 | 112.0 | 142.0 | 152.3 | 155.7 | 156.5 | 157.3 | 158.1 |

4.2 The displacement process of natural gas
Analysis of equation (18) shows that the efficiency of displacement decreases with the increase of system
temperature. It is proved that the displacement process is an exothermic reaction according to the thermodynamic reaction law. So, the displacement reaction will move forward with the temperature of the system decreases, increasing the efficiency of displacement. The methane efficiency of carbon dioxide displacement at different temperatures through hydrate displacement experiments can be obtained by experiment, as shown in Table 7.

Table 7: the efficiency of displacement diagram of carbon dioxide at 5.8MPa.

| Temperature (°C) | 274.0 | 274.5 | 275.0 | 275.5 | 276.0 | 276.5 | 277.0 | 277.5 | 278.0 | 278.5 |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Traditional (%) | 8.70  | 13.56 | 18.46 | 22.40 | 24.65 | 25.95 | 26.43 | 26.91 | 27.26 | 27.24 |
| New model (%)   | 8.89  | 14.41 | 20.43 | 25.21 | 26.51 | 26.99 | 27.09 | 27.12 | 27.19 | 27.91 |

It can be seen from the diagram that the displacement process increases firstly and then decreases with the increase of temperature. This is because that the efficiency of displacement is defined as the ratio of the decomposition amount of methane to the total content of methane in the pre-reaction hydrate system during the displacement. In the course of the experiment, the thermal degradation of natural hydrates cannot be avoided because of the change of temperature, which leads to the inaccurate calculation of displacement efficiency under real conditions. As the diagram shows, the efficiency of carbon dioxide displacement is lower when the temperature of the system is low. This is because the carbon dioxide injected into the system is easily adsorbed on the surface of the natural gas hydrate to form a layer of carbon dioxide hydrate film at the beginning of the reaction. When the temperature rises to a certain level, that is, the decomposition temperature of carbon dioxide hydrate, the carbon dioxide hydrate formed by displacement reaction will be decomposed, resulting in the reduction of displacement efficiency.

5. Conclusion
At present, there are some problems such as low displacement efficiency in the process of gas hydrate extraction. Under internal conditions, the efficiency of displacement is improved to a certain extent by changing the injection form of carbon dioxide that changing gaseous carbon dioxide into emulsion. The pyrolysis of natural gas hydrate can be improved by changing the temperature and pressure of the reaction system under external conditions, destroying the film formed by carbon dioxide molecules on the surface of natural gas hydrate, which increasing the contact area between carbon dioxide and hydrate, leading to a higher displacement efficiency. In field applications, the pressure of the reaction system is often changed by changing the amount of carbon dioxide injected, which requires high pressure injection equipment and high voltage line. Compared to the temperature, the displacement process is more sensitive to temperature and easy to operate in the field. Therefore, it is suggested that the displacement efficiency can be changed by changing the temperature during site construction.

By analyzing the influence of temperature on the ratio of gas volume, the new model of displacement degree with temperature was deduced, and the efficiency of displacement reaction was obtained under different temperature conditions. On the one hand, increasing the temperature can increase the methane gas production; however, it will lead to the decomposition of carbon dioxide hydrate when the temperature rises above the phase equilibrium temperature of carbon dioxide hydrate. On the other hand, increasing the temperature of the reaction system is not entirely conducive to the occurrence of displacement reaction in conventional contact heat exchange. According to the third law of thermodynamics, the cost of heat exchange will increase when the difference of temperature increases. The more serious the heat loss, the less economic benefit can get. In this paper, the optimum temperature of displacement system with higher displacement efficiency can be obtained by studying the changing law of displacement reaction with temperature.

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