

Original article

Hydrate dissociation induced by gas diffusion from pore water to drilling fluid in a cold wellbore

Youhong Sun¹, Hongfeng Lu², Cheng Lu², Shengli Li^{1*}, Xiaoshu Lv³

¹Key Laboratory of Drilling and Exploitation Technology in Complex Conditions of Ministry of Land and Resources, College of Construction Engineering, Jilin University, Changchun 130026, P. R. China

²Guangzhou Marine Geological Survey, China Geological Survey, Guangzhou 510075, P. R. China

³Department of Civil and Structural Engineering, School of Engineering, Aalto University, PO Box 12100, FIN-02015, Finland

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Corresponding author:

*E-mail: lishengli@jlu.edu.cn

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Abstract:

It is a common view that the high temperature of the drilling fluid can lead to the dissociation of gas hydrate during drilling through hydrate-bearing sediments. This study indicates that the hydrate dissociation in wellbore can also be induced by gas diffusion from pore water to drilling fluid even if the temperature (and the pressure if necessary) of the drilling fluid is well controlled to keep the conditions of hydrate-bearing sediments along the hydrate equilibrium boundary. The dissociation of gas hydrate was modelled based on Fick's first law. It was found that the dissociation rate mainly depended on the temperature of the sediments. The locations of dissociation front of CH₄ hydrate and CO₂ hydrate in wellbore were calculated as a function of time. The impacts of the hydrate dissociation on the wellbore stability and the resistivity well logging in sediments were evaluated.

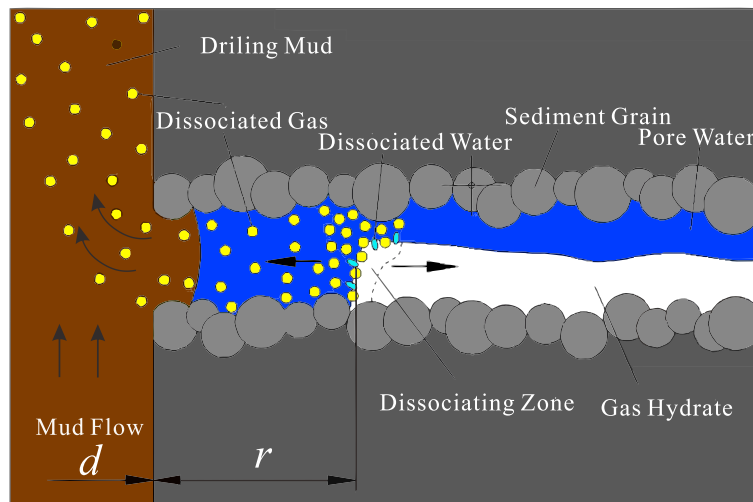
1. Introduction

Gas hydrates is widely distributed all around the world and has been accepted as a potential strategic energy form (Song et al., 2014). The exploration and exploitation of marine gas hydrates have become hot topics in current and future energy research. Well drilling is a key step for gas hydrate exploration and for most techniques (Liu et al., 2012; Liu et al., 2017; Cui et al., 2018) to extract gas contained within natural gas hydrate sediments (Wang et al., 2014). However, the high temperature of the drilling fluid and heat generated from the drilling tool friction can cause the dissociation of hydrates in sediments in the drilling process (Kwon et al., 2010; Ning et al., 2013). If gas hydrates dissociate, the mechanical and physical properties of the sediments will change and the mechanical failure can cause the instability of wellbore (Winters et al., 2007), especially for soft, fine-grained, mud-dominated hydrate-bearing sediments with poor degree of consolidation,

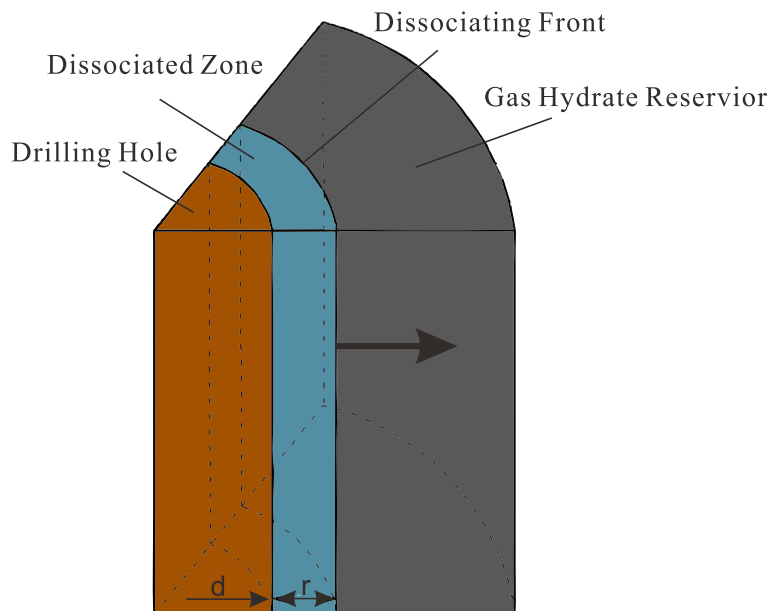
such as at some sites on the Indian continental margin and in the South China Sea where the sediments are cemented by hydrates. It is essential to pay attention to the prevention of hydrate dissociation in borehole (Freij-Ayoub et al., 2007; Kwon et al., 2010; Khabibullin et al., 2011).

Efforts have been made to improve the hydrate drilling conditions. Freij-Ayoub et al. (2007) used numerical modelling to quantify the risk of drilling a wellbore through hydrate-bearing sediments, which showed that the control of pressure and temperature in wellbore is a practical way to mitigate the risks of drilling in hydrate bearing strata. Ning et al. (2013) suggested a method to reduce this risk by maintaining the wellbore pressure at a higher level than the pore pressure. Zhao et al. (2010) proposed a mud cooling technology for drilling operation in hydrate bearing strata. A mud cooling system was tested both in laboratory and in gas hydrate drilling field. Then, if the pressure and temperature in wellbore are controlled by the technologies mentioned above, the conditions of hydrate-





(a) Gas diffusion and hydrate dissociation in a pore channel



(b) Hydrate dissociation front moving in the hydrate-bearing sediments

Fig. 1. Schematic diagram of hydrate dissociation induced by gas diffusion from pore water to drilling fluid.

bearing sediments near the wellbore can be kept above the equilibrium. Therefore, no hydrate dissociation caused by pressure drop, temperature rise or even high concentration of salts in drilling fluid will happen. Nevertheless, while drilling, hydrate dissociation that induced by gas diffusion from pore water in hydrate-bearing sediments to drilling fluid in wellbore cannot be stopped.

As can be seen from Fig. 1, the drilling fluid circulates between wellbore and the mud pool on the ground while the pore water keeps still in hydrate-bearing sediments. The fluid and pore water are interconnected within the porous structure of sediments in the wellbore. However, the concentration of gas dissolved in the pore water is higher than that in the drilling fluid based on the following facts. First, equilibrium

calculations show that the pore water in contact with solid gas hydrates must contain higher concentration of gas depending upon the specifics of temperature, pressure, and gas composition (Tishchenko et al., 2005; Zhang et al., 2011). Second, the gas concentration in the drilling fluid is kept at a very low level far from saturated as the drilling fluid flows upward to the ground to desorb the gas continuously. Undoubtedly, there will be a mass transfer of dissolved gas from pore water to the fluid through the pore channels. Once the gas concentration in the pore water is lower than the equilibrium solubility, hydrate will dissociate and release gas to the pore water (Nimblett et al., 2003). During such drilling, the hydrate in the wellbore keeps dissociating due to the gas diffusion and transportation to the ground by drilling fluid. Different from hydrate dissociation in

depressurization (Liu et al., 2017), the dissociation is confined in a very narrow region. The dissociation of hydrate is confined in a very thin ring around the wellbore that the front starts to move until no hydrate remains in the ring. Then there is no hydrate exists in sediments between the wall to the dissociation front that the mechanical strength of the sediments may drop heavily.

Recent studies about drilling safety focused on the hydrate decompositions that were caused by invasion of the drilling mud into sediments (Ning et al., 2013), pressure drop, temperature rise (Kwon et al., 2010) and thermodynamic inhibitors such as salts (Hao, 2011). However, there are no researches concerning the hydrate dissociation induced by gas diffusion from pore water in hydrate-bearing sediments to drilling fluid in a cold wellbore. It was not sure whether the diffusion driven dissociation of hydrates could also cause the instability of wellbore and affect the reliability of geophysical resistivity well logging (Hyndman et al., 1999). In fact, an experimental study on this issue is quite difficult as a dynamic setting should be established. In this work, the kind of hydrate dissociation kinetics was studied by proposing a diffusion model. To evaluate the impacts of hydrate dissociation, the location of dissociation front was calculated as a function of time and the key factors were analyzed based on the model.

2. Modelling

In this study, it is assumed that the drilling fluid is well pressure-controlled and cooled during the drilling process. The conditions of hydrate-bearing sediments are kept equal to or higher than that of hydrate equilibrium. In addition, in nature, vast quantities of hydrate in sediments are formed from dissolved-phase gas of pore fluids upward flowing into the hydrate stability field (Hyndman and Davis, 1992; Spangenberg et al., 2005; Waite and Spangenberg, 2013). Free gas rarely existed in this kind of hydrate-bearing sediments. The following are a summary of the assumptions made for the diffusion model:

- The temperature of the drilling fluid is the same as that of the hydrate-bearing sediments, and hence there is no heat transfer from the drilling fluid to the sediments.
- The pressure of the drilling fluid is kept higher than that of the hydrate-bearing sediments.
- Two-phase equilibrium is supposed to be existing in the sediments: Hydrate phase and pore water phase without free gas.

In this way, the drilling fluid invades into the bore wall with filter cake (Ning et al., 2013). The pore water with high gas concentration connected with the drilling fluid. The mass transfer of gas from gas hydrates to drilling fluid can be divided into three steps:

- The diffusion of dissolved gas from pore water to drilling fluid under the driving force of concentration difference.
- The drilling fluid flows to the pool on the ground to desorb the gas obtained in the first step.
- Due to the drop of gas concentration in the pore water in the first step, hydrates dissociate to release gas to pore water

for the loss of gas and the dissociation front moves forward in sediments.

As the drilling fluid flows fast in the wellbore, the gas in the fluid can be desorbed very soon. In addition, the gas concentration in pore water can be immediately recovered by a small amount of hydrate dissociation. In this case, the hydrate dissociation process is induced and controlled by the first step. In the first step, it is simplified that the dissolved gas diffuses in a one-dimensional and horizontal pore channel; And the gas hydrates in the channel are continuous based on an average view (As shown in Fig. 1(a)). Then the diffusion of gas dissolved in pore water into drilling fluid can be modelled using the Fick's first law of diffusion equation (Guo et al., 2013):

$$J = -D \frac{\Delta C}{\Delta r} \quad (1)$$

where J is the molar flux of gas diffusing through unit area of pore in the wellbore, D is the diffusion coefficients of gas in the pore water phase, Δr is the distance between the wellbore to the dissociation front (see Fig. 1, hydrate dissociation takes place within a narrow cylindrical zone), and ΔC is the concentration difference between the pore water (C_w) and the drilling fluid (C_f) that is lower enough to be neglected. As C_w is the equilibrium solubility of the guest in pore water in equilibrium with the hydrate according to the pressure and temperature of the sediments, ΔC is a constant that do not change with the time.

The volumetric rate of hydrates dissociation in the hydrate-bearing strata field is formulated as:

$$\frac{dV_h}{dt} = \frac{J \cdot 2\pi(r_0 + r)L \cdot \phi_s \cdot (M_g + NM_w)}{\rho_h} \quad (2)$$

where V_h is the cumulative volume of hydrate that has dissociated at time t , $2\pi(r_0 + r)L$ is the cylindrical area of the dissociation front in sediments, L is the thickness of hydrate-bearing sediments, ϕ_s is the surface porosity of the dissociation front, M_w and M_g are the molar masses of the water and guest substance, N is the hydration number of 6.0 (when sI hydrate cavities are fully occupied by gas molecules, hydration number is 5.75), the ratio of the number of water molecules to that of guest molecules in the hydrate, and ρ_h is the mass density of the hydrate (0.912 g/cm³ for sI hydrates) (Gabbito and Tsouris, 2010).

The volume of hydrate-bearing sediments (V) that holding the hydrates dissociated is:

$$V = \frac{V_h}{S_h \phi_b} \quad (3)$$

where S_h is the hydrate saturation in the sediments, and ϕ_b is the bulk porosity of the sediments.

By combining Eqs (1), (2), and (3), we can obtain the following equation:

$$rdr = \frac{D \cdot \Delta C \cdot (M_g + NM_w) \cdot \phi_s}{\rho_h S_h \phi_b} dt \quad (4)$$

For simplicity, the following relationship is applied:

$$\phi_s = \phi_b \quad (5)$$

Integrating Eq. (4), we obtain:

$$r = kt^{1/2} \quad (6)$$

$$\text{where } k = \left(\frac{2DC_w(NM_w + M_g)}{\rho_h S_h} \right)^{1/2}$$

As the dissolved gas diffuses from pore water to the drilling fluid, hydrates in pore water keep dissociating and the dissociation front moves to the hydrate-bearing sediments around the wellbore. Eq. (6) can be used to describe the relationship between the location of hydrate dissociation front and the time.

3. Results and discussion

The model shows that the moving rate of the hydrate dissociation front is affected by several parameters, including the guest substance, the diffusion coefficients, the solubility of the guest molecules in pore water and the hydrate saturation in the sediments. As reviewed by Kvenvolden (1995), methane in subaquatic settings from around the world is mainly derived by the microbial reduction of CO₂ from sedimentary organic matter. Natural CO₂ hydrate deposits have been observed at a number of locations, including Minami-Ensei Knoll (695-705 m), Iheya North Knoll (970 m), Yonaguni Knoll IV (1,370-1,385 m), the JADE hydrothermal field (1,300-1,450 m), and Hatoma Knoll (~1,500 m) in the Okinawa Trough, and have been inferred to exist in the subsurface at the Champagne Vent site (1,604 m) on the Mariana Arc (Hou et al., 1999; Inagaki et al., 2006; Lupton et al., 2013). When drilling through hydrate-bearing sediments, the dissociation of both CO₂ hydrate and CH₄ hydrate in wellbore should be considered. In this work, by applying the diffusion model obtained in Eq. (6) to the drilling process of the two hydrate-bearing sediments, the expanding rates of the hydrate dissociation front in sediments were studied.

With respect to the hydrate equilibrium conditions controlled in ocean drilling, the pressure and the temperature were selected from the hydrate equilibrium line calculated by Chen-Guo model (Chen and Guo, 1996; Chen and Guo, 1998) and shown in Table 1. Different hydrate equilibrium conditions correspond to different depth of hydrate-bearing sediments.

3.1 CH₄ hydrate

It was found that the diffusion coefficients of methane in water depended on the temperature (Guo et al., 2013). At a constant temperature, pressure has very small effect on the diffusion coefficients. The relationship between diffusion coefficient of methane in water [$D(\text{CH}_4)$ in m²/s] and temperature (T in K) can be described by Speedy-Angell power-law, (Guo et al., 2013) i.e.,

$$D(\text{CH}_4) = D_0 \left(\frac{T}{T_s - 1} \right)^m \quad (7)$$

Table 1. The diffusion coefficients and solubility of dissolved CH₄ calculated under different methane hydrate equilibrium conditions (Tishchenko et al., 2005; Guo et al., 2013).

T (K)	P (MPa)	D (10^{-9} m ² /s)	C_w (mol/kg)
274.0	2.76	0.72	0.060
281.0	5.76	0.95	0.093
288.0	12.63	1.21	0.138

where $D_0 = 5.95 \times 10^9$ m²/s, $T_s = 229.8$ K, $m = 1.8769$.

In the presence of hydrate in pore water, the solubility of methane was calculated according to the equations established by Tishchenko et al. (2005). The equation shows that the solubility of methane is also dependent on the temperature when hydrate is stable. The hydrostatic pressure and salinity of water had relatively small effects on the solubility of methane (See Fig. 2). Then the gas concentrations in pore water at different depth have little difference. Gas diffusion in upward direction can be neglected. This is why only radial diffusion is considered in the model.

Both the diffusion coefficients and solubility of dissolved methane in pore water under the three hydrate equilibrium conditions were calculated (Tishchenko et al., 2005; Guo et al., 2013) and shown in Table 1. The distance between CH₄ hydrate dissociation front and wellbore, r , were calculated according to Eq. (6) at the three specified temperatures. The results are shown in Fig. 3. Figs. 3(a)-3(c) show that, in sediments with a certain hydrate saturation, the hydrate dissociation front evolves with time. The moving rate is faster at higher temperatures when the diffusion coefficient and the solubility of CH₄ in the pore water are bigger. It should be noted that the concentration of gas in water in equilibrium with gas hydrate increases with the increasing temperature (Fig. 2) (Tishchenko et al., 2005). There is a contrary trend in the water without gas hydrate. At the same time points and specified temperature, the distance between the hydrate dissociation front and the wellbore, r , decreases with the increase of hydrate saturation. As the consumption of gas is diffusion-controlled, higher hydrate saturation means larger amount of gas for consumption, indicating that the dissociation front moves slower in sediments with higher hydrate saturations. Fig. 3(d) shows the variations of the location with the hydrate saturation at different temperatures after 240 h (Results of longer time scale may also have reference value for long horizontal wells). The distances range from 0.5 cm to 2 cm at different hydrate saturation and temperature. It is concluded that hydrate dissociation front moves faster in hydrate-bearing sediments with lower hydrate saturations and higher temperatures. Since the dissociation of hydrate is induced by gas diffusion, the movement of hydrate dissociation front in hydrate-bearing sediments is controlled by gas diffusion rate. At higher temperatures, there are higher driving force of concentration gradient and higher diffusion coefficients, which lead to higher gas diffusion rate. Then

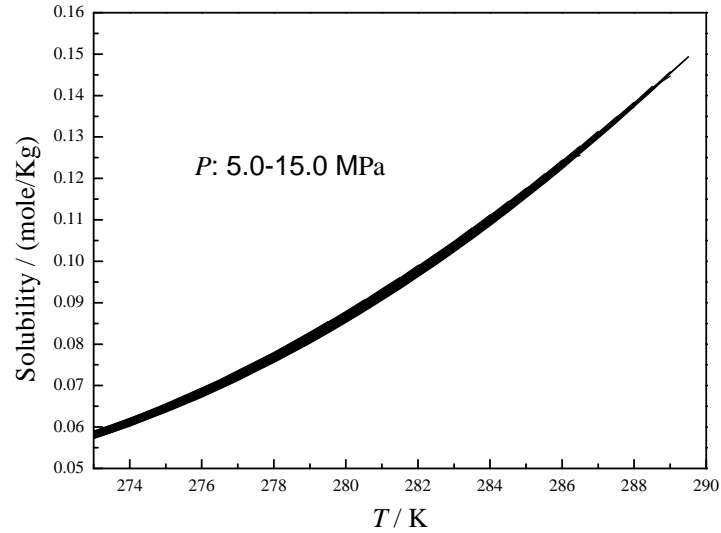


Fig. 2. Solubility of methane in water equilibrium with hydrate in a pressure range of 5.0 to 15.0 MPa (Tishchenko et al., 2005; Guo et al., 2013).

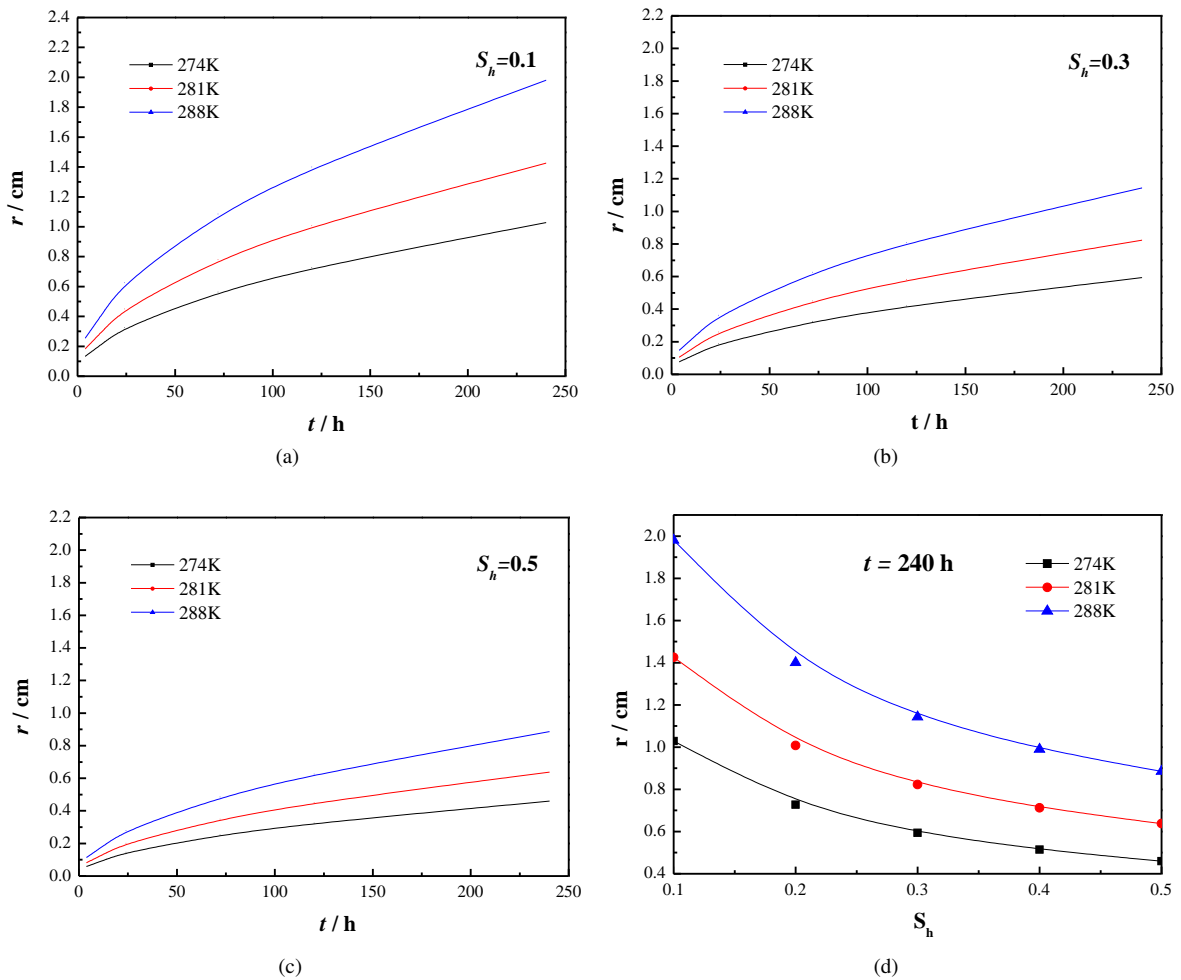


Fig. 3. (a)-(c) Variations of the location of CH_4 hydrate dissociation front, r , with the time. (d) After 240 h, the location of CH_4 hydrate dissociation front in sediments with different hydrate saturations and temperatures.

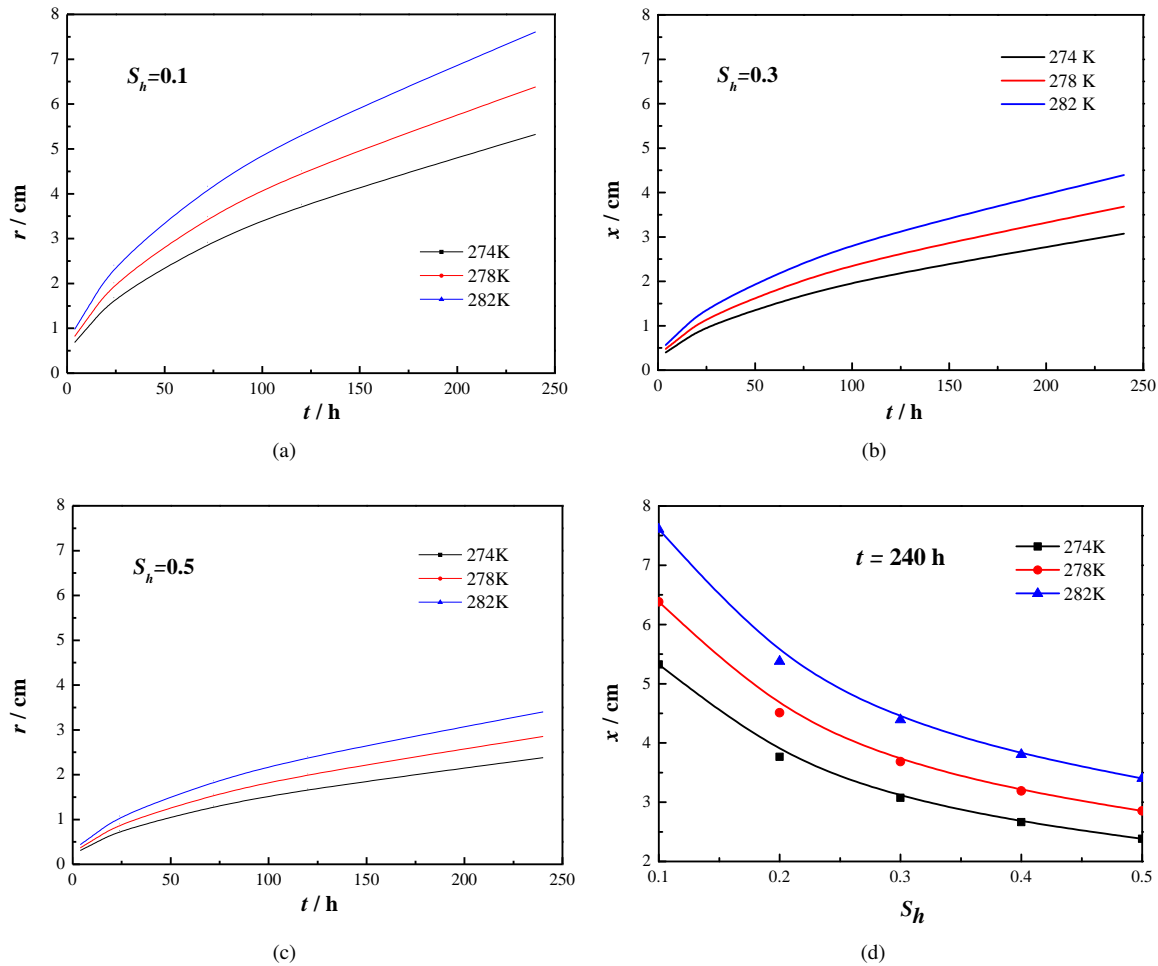


Fig. 4. (a)-(c) Variations of the location of CO₂ hydrate dissociation front, r , with the time. (d) After 240 h, the location of CO₂ hydrate dissociation front in sediments with different hydrate saturations and temperatures.

hydrate dissociation front moves faster at higher temperatures. Therefore, the temperature in the mud cooling system applied should be set to a low value to maintain a low temperature condition of hydrate-bearing sediments near the wellbore.

3.2 CO₂ hydrate

For CO₂+H₂O system, the pressure also showed little influence on CO₂ diffusion coefficient (Frank et al., 1996; Azin et al., 2013). The diffusion coefficients of CO₂ in water can be correlated using Arrhenius-type equations (Frank et al., 1996):

$$D = 1.81 \times 10^{-6} \exp\left(\frac{-16900}{RT}\right) \quad (8)$$

The solubility of CO₂ in pore water contacting with CO₂ hydrate was calculated by the method proposed by Duan (Duan and Sun, 2003; Duan et al., 2006; Li and Duan, 2007). The dependence of the solubility of CO₂ on the temperature was also confirmed and the effects of the pressure were small.

The diffusion coefficient and solubility of CO₂ in pore water under specified hydrate equilibrium conditions were calculated and shown in Table 2. The locations of CO₂ hydrate

Table 2. The diffusion coefficients (Frank et al., 1996) and solubility of dissolved CO₂ (Duan and Sun, 2003; Duan et al., 2006; Li and Duan, 2007) calculated under different CO₂ hydrate equilibrium conditions.

T (K)	P (MPa)	D (10^{-9} m ² /s)	C_w (mol/kg)
274.0	1.38	1.09	0.903
278.0	2.20	1.21	1.168
282.0	3.65	1.34	1.499

dissociation front, r , were calculated by using Eq. (6) and shown in Fig. 4. It was found that the variations of r over time at different temperatures have similar trend as that for CH₄ hydrate. The temperature and hydrate saturation had the same influences on the moving rate of hydrate dissociation front. However, the difference is that the moving rates of CO₂ hydrate dissociation front were much higher than that of CH₄ hydrate. As can be seen from Fig. 4(d), after 240 h, the distances range from 2.5 to 7.6 cm at different hydrate saturations and temperatures. This is mainly due to the higher

solubility of CO₂ than that of CH₄ in the pore water at the same temperature.

It is known that hydrate dissociation can result in a remarkable reduction in the mechanical strength of sediments and affect resistivity well logging in the gas hydrate-bearing sediments (Hyndman et al., 1999; Waite et al., 2008). In this study, hydrate dissociated zone caused by gas diffusion is now found much smaller than that of partial hydrate dissociation caused by the invasion of mud and temperature disturbance (Kwon et al., 2010; Ning et al., 2013). Although dissociation of hydrate in dissociated region is complete, the region dissociated is very thin. Even if CH₄ hydrate dissociation results in borehole wall failure, a hole enlargement of 1-2 cm will not cause possible instability of the wellbore and distort in resistivity well logging during drilling. However, when drilling through CO₂ hydrate-bearing sediments (Hashimoto et al., 1995; Hou et al., 1999; Inagaki et al., 2006; Lupton et al., 2006), the impacts of diffusion induced dissociation will be larger due to the higher solubility that closer attention may be paid to the stability of the borehole even in a cold wellbore. In summary, hydrate dissociation induced by gas diffusion does not pose a significant wellbore stability risk in a cold drilling through hydrate-bearing sediments. Temperature-controlled technologies like mud cooling system can work well in keeping wellbore stable during drilling through hydrate-bearing sediments.

4. Conclusions

It was proposed that hydrate dissociation could be induced by gas diffusion from the pore water to the drilling fluid in a cold wellbore. A kinetic model was developed to study the diffusion driven dissociation. The location of the hydrate dissociation front was calculated for CH₄ and CO₂ hydrate-bearing sediments as a function of time. As the gas diffusion coefficient and solubility in pore water equilibrium with hydrate increased with the increase of temperature, the moving rate of gas hydrate dissociation front was mainly increased with the increase of the temperature in sediments. It demonstrated the impacts of hydrates dissociation on the wellbore stability in a cold drilling and on the resistivity well logging were not significant.

Nomenclature

J = molar flux of gas diffusing through unit area of pore in the wellbore

D = diffusion coefficients of gas in the pore water phase

Δr = distance between the wellbore to the dissociation front

ΔC = concentration difference between the pore water and the drilling fluid

C_w = concentration of gas in the pore water

C_f = concentration of gas the drilling fluid

V_h = cumulative volume of pure hydrate that has dissociated at time t

t = dissociated time

L = thickness of hydrate-bearing sediments

ϕ_s = surface porosity of the dissociation front

M_w = molar masses of the water

M_g = molar masses of the guest substance

N = hydration number

ρ_h = mass density of the hydrate

S_h = hydrate saturation in the sediments

ϕ_b = bulk porosity of the sediments

k = dissociation constant

Subscripts

h = hydrate

w = water

g = gas

f = drilling fluid

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