

Effect of electrolytes on the self-protection of natural gas hydrate decomposition

Haixiang Zhang^{1,2}, Jinze Xu^{3,*}, Zhandong Li^{1,2,4}, Xin Tian⁵, Wenbo Meng⁶ and Dianju Wang^{1,2}

¹ Heilongjiang Key Laboratory of Gas Hydrate Efficient Development, Heilongjiang DaQing 163318, China

² College of Offshore Oil and Gas Engineering, Northeast Petroleum University, Heilongjiang DaQing 163318, China

³ Department of Chemical and Petroleum Engineering, University of Calgary, Calgary T2N 1N4, Canada

⁴ Sanya Offshore Oil & Gas Research Institute, Northeast Petroleum University, Hainan Sanya 572025, China

⁵ College of Petroleum Engineering Institute, Northeast Petroleum University, Heilongjiang DaQing 163318, China

⁶ China National Offshore Oil Corporation Hainan Branch, Haikou 570000, China

* Corresponding author: Jinze Xu. E-mail: jinze.xu@foxmail.com

Received 30 December 2020, revised 11 April 2021

Accepted for publication 7 June 2021

Abstract

This paper presents an experimental study of methane hydrate decomposition with different concentrations of electrolytes Na⁺ and K⁺, with the aim of exploring the electrolyte's behaviour characteristics shown in its effect on the self-protection effect of methane hydrate during decomposition. The study used an experimental device for hydrate synthesis and decomposition. It focuses on the effect of electrolytes on the self-protection effect of methane hydrate during the self-protection effect during methane hydrate decomposition. (i) Na⁺ ions have an inhibitory effect on self-protection, whereas K⁺ ions do not have a significant effect. (ii) There is a negative correlation between the hydrate self-protection effect and the concentration of Na⁺ ions. However, an excessive Na⁺ concentration can inhibit the hydrate gas production rate. (iii) The synergistic system of Na⁺ and K⁺ ions has a better inhibitory effect on the hydrate's self-protection effect than a single Na⁺ ion solution. As the concentration of the synergistic system increased, the hydrate gas production rate was not inhibited. However, in contrast to a single Na⁺ ion solution, when the concentration of the synergistic system was too high, the methane hydrate gas production rate was not inhibited because of the coexistence of cations.

Keywords: methane hydrate, electrolyte, self-protection effect, Na⁺ ion, K⁺ ion, synergy

1. Introduction

Natural gas hydrate, also known as hydrate, is a unique resource with many advantages, such as less pollution, large energy per unit volume and abundant geological reserves. Therefore, it is considered as a future energy source (Milkov 2004, Sloan & Koh 2007, Wang *et al.* 2020; Xuan *et al.* 2018; Luo 2013). So far, few reports have discussed the effect of electrolytes on hydrate decomposition, especially the effect of different ion solutions on the hydrate's self-protection.

Worldwide research on the self-protection effect during hydrate decomposition is abundant. For instance, Handa (1986) found through experiments that gas hydrates showed an unusual stabilisation in a non-equilibrium state below the freezing point. Handa named it 'lattice stabilisation.' To verify this phenomenon, Gudmundsson (1990) performed a decomposition experiment by storing hydrates in storage tanks with good thermal insulation. Hydrates were in a metastable state during decomposition and could maintain their stability for a long period (for more than an hour).

Later, Yakushev (1989) carried out a decomposition experiment of methane hydrate under atmospheric pressure. He proposed that an ice layer would form at the surface during the decomposition process, which could effectively prevent methane hydrate from decomposing and be maintained for months or years under atmospheric pressure and a specific condition at sub-zero temperature. In addition, Stern *et al.* (2001) conducted a large number of decomposition experiments on pure methane hydrate at atmospheric pressure through a rapid decompression method and temperature delay method, which also proved that the hydrate self-protection phenomenon was in a metastable state. Since then, many scholars have studied the self-protection effect during hydrate decomposition. Through experiments, Kamath proved that the production of hydrate through the brine injection method has a higher gas production rate and energy efficiency than the steam injection method (Kamath & Godbole 1987). Tang *et al.* (2006) conducted experiments on natural gas hydrate production through hot brine injection and summarised the changes in parameters during the experiment, including gas production, water production and temperature. This study verified the effect of electrolytes on hydrate decomposition. Later, Li *et al.* (2012) proposed the influence of hot brine injection speed, temperature and time on energy efficiency through an orthogonal experiment. However, this study did not explain the effects of different electrolytes and electrolytes on hydrate decomposition.

With the development of technology, scholars have explored the essence of the hydrate's self-preservation effect from a micro-scale perspective, which was compared to the initial macro-scale observations, physical property tests and experiments. For instance, Takeya *et al.* (2002) used X-ray diffraction technology to measure the decomposition rate of hydrate in different temperature zones, and proposed that the 'self-preservation' effect of hydrate mainly depended on the diffusion rate of methane on the ice surface. However, this idea failed to consider particle size changes during hydrate decomposition. Ebinuma *et al.* (2008) monitored the complete decomposition process of hydrate sediments using X-ray computed tomography. On this basis, Nagao *et al.* (2008) used scanning confocal microscopy to monitor the change in hydrate thickness during the decomposition process (Guo *et al.* 2009). This study suggested that the existence of the 'self-preservation effect' would cause the thickness of hydrate ice to increase again. Using neutron diffraction technology, Uchida *et al.* (2011) proposed that the gas composition, sample size and the amount of pre-generated ice also affected the 'self-preservation effect.' Studies have shown that various factors can affect the self-preservation effect of hydrates and that the self-preservation effect indeed exists.

According to existing research, only a few scholars have studied the influence of electrolytes on the self-protection effect during hydrate decomposition (Uchida *et al.* 2011; Li

et al. 2020; Song *et al.* 2009). Relative research has mainly focused on the hydrate synthesis stage (Kashchiev 2000; Stern *et al.* 2001). Moreover, because of the limitations of the experimental method, these studies were unable to explain the mechanism clearly. Several key scientific problems regarding the influence of the electrolyte on the self-protection effect during gas hydrate decomposition remain unsolved. First, the existence of the electrolyte in the hydrate affects the hydrate decomposition characteristics. Second, if electrolytes can promote or inhibit hydrate decomposition, which electrolyte(s) are effective remains unknown. Third, whether the electrolytes in a synergistic system can change the hydrate decomposition behaviour compared to a single electrolyte. Therefore, based on previous research results, hydrate formation and decomposition experiments under different electrolytes were carried out using a self-developed visualisation experimental device for hydrate formation and decomposition, and the characteristics and laws of the electrolyte influencing the hydrate self-protection effect were analysed in combination with relevant experimental rules. This study is expected to provide a theoretical basis for efficiently optimising the production method of natural gas hydrate and determining the optimal production time.

2. Experimental equipment and methods

2.1. Experimental equipment and materials

2.1.1. Experimental equipment. A self-made experimental device for hydrate formation and decomposition was used in this experiment (figure 1). The device mainly consisted of four parts: gas inlet and outlet system, temperature and pressure control system, hydrate formation and decomposition system, and a visual system. The equipment and flow chart are presented in figure 1. In this system, the reactor was a 500-ml cylinder with a maximum operation pressure of 50 MPa. A PT100 (Omega Engineering) temperature sensor with an error of $\pm 1^\circ\text{C}$ of the temperature control system and a control range of -40 – 100°C . The reactor was equipped with a pressure sensor with an accuracy of ± 0.01 MPa and a measuring range of 0 – 40 MPa. The temperature sensor and pressure sensor monitored the temperature and pressure changes at the inlet and outlet of the reactor, respectively. A high-precision gas flowmeter was set at the outlet of the reactor, with a minimum accuracy of $0.001\text{ cm}^3\text{ s}^{-1}$ and a response time of ≤ 0.5 s to monitor the gas output and flow rate. To reduce the heat exchange between the environment and the reactor as much as possible, the reaction had a thermal protective coating on its external surface. This device achieves the stimulation of hydrate synthesis and decomposition by changing the initial pressure and temperature inside the reactor. Experimental data were collected and output through

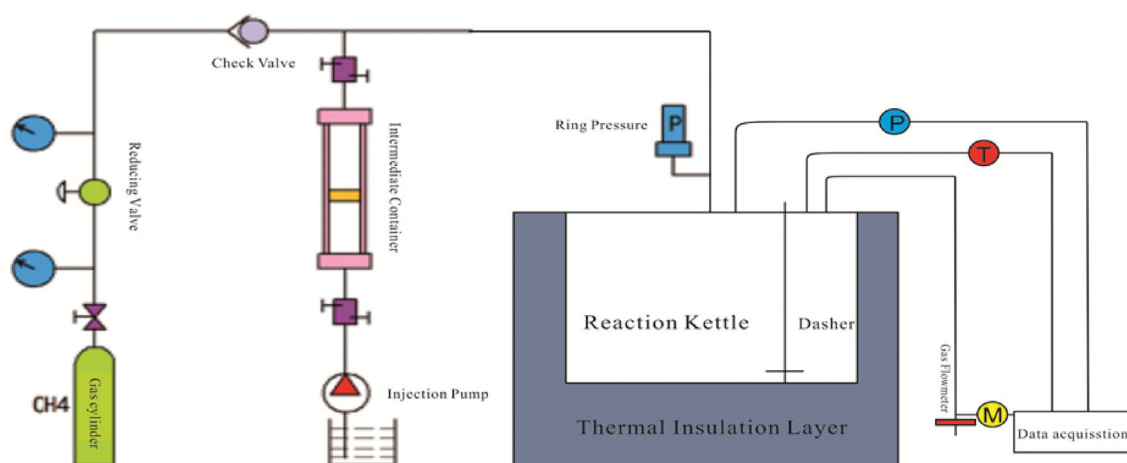


Figure 1. Experimental apparatus for formation and decomposition of natural gas hydrate.

Table 1. Experimental materials and reagents

Material	Specification	Manufacturer	Notes
Methane	Purity: $\geq 99\%$	Tianjin Kemiou chemical reagent	
Deionised water	High purity	Made in laboratory	
Sodium chloride	Purity: $\geq 99\%$	Tianjin Kemiou chemical reagent	
Potassium chloride	Purity: $\geq 99\%$	Tianjin Kemiou chemical reagent	
Glass container	Volume: 500 ml		
Electrolyte synergistic system		Made in laboratory	Sodium chloride, potassium chloride

the monitoring system to the computer to achieve real-time monitoring.

2.1.2. Experimental materials. According to previous research on hydrate sediments, a large number of electrolyte ions exist in natural gas hydrates. Egeberg *et al.* found that there were a large number of cations, including K^+ , Na^+ and Ga^{3+} , in the gas hydrate sediments, among which K^+ and Na^+ account for more than 60% (Egeberg & Dickens 1999; Li *et al.* 2020). Yang and Liu have proved through an orthogonal test that Cl^- does not affect the phase equilibrium of hydrate (Yang & Liu 2009). Therefore, in this study, sodium chloride and potassium chloride were used as electrolyte solutions.

Part of the experimental materials were prepared in the laboratory. The gas used in this experiment was methane with a purity of over 99%. The liquid was high-purity deionised water and the electrolytes were sodium chloride and potassium chloride with a purity of over 99%. The synergistic system was a mixture of NaCl and KCl. The experimental materials and reagents are listed in Table 1.

2.2. Experimental approach

2.2.1. Experimental conditions. In this experiment, Na^+ and K^+ solutions with concentrations of 0, 0.5, 1, 1.5 and 2%

were used for the hydrate decomposition experiment with the aim of analysing the influence of different electrolytes at different concentrations on the hydrate self-protection effect during decomposition. The experiment also used a synergistic system solution with concentrations of 0, 0.6, 1, 1.6 and 2.1% to observe the influence of electrolytes in different synergistic systems on the hydrate self-protection effect during its decomposition. The specific experimental conditions are presented in Table 2.

2.2.2. Experimental procedure.

- (1) The electrolyte solution and synergistic system solution was prepared with pure sodium chloride, potassium chloride and deionised water in the laboratory. The wall of the reactor and the inner and outer walls of the plastic container were washed with deionised water to prevent impurities and residual moisture from interfering with the experiment. At the same time, the incubator was heated to $40^\circ C$ and heated for 20–30 more minutes to keep the incubator dry.
- (2) The temperature and pressure sensors were tested and calibrated. After the incubator was completely dry, the video collector was opened, the electron microscope was adjusted until the video was clear and the incubator was closed to collect the reaction video.

Table 2. Experimental conditions

Scheme no.	Na ⁺ concentration	K ⁺ concentration	Concentration of the synergistic system solution (%)		Initial pressure (MPa)	Initial temperature (°C)
			Na ⁺	K ⁺		
S1	0	0	0	0	8.4	2
S2	0.5	0.5	0.5	0.1	8.4	2
S3	1.0	1.0	1.0	0.1	8.4	2
S4	1.5	1.5	1.5	0.1	8.4	2
S5	2.0	2.0	2.0	0.1	8.4	3

- (3) Next, the injection valve was opened to inject 490 ml of electrolyte solution with 0% Na⁺ into the reactor, and then inject 10 cm³ of methane gas into the reactor, keeping the pressure constant at 8.4 MPa and the temperature at 2°C until the hydrate was completely synthesised.
- (4) After the hydrate was completely synthesised, the next step was hydrate decomposition by depressurisation. The outlet valve was opened at the outlet end, the pressure was slowly adjusted from 8.4 to 1.5 MPa, then remained constant at 1.5 MPa for about 0.5 h to avoid incomplete hydrate decomposition, which can result in low gas production.
- (5) At the same time as step (4), the gas flowmeter was turned on and the gas production change during decomposition was recorded. When the reading gradually stabilised, the gas outlet valve was closed and the gas production volume was recorded. In this experiment, the peak period of hydrate decomposition lasted approximately 5 s, but each group of hydrates took a long time (more than 1 h) before it completely decomposed.
- (6) The 14 experiments used Na⁺ solutions with concentrations of 0.5, 1, 1.5 and 2%; K⁺ solutions with concentrations of 0.5, 1, 1.5 and 2%; and a synergistic system solution with concentrations of 0, 0.6, 1, 1.6 and 2.1%. All these experiments followed the experimental steps (1)–(5).

3. Results and analysis

3.1. Features of self-protection effect during decomposition

The self-protection effect occurs during the entire decomposition period (Volmer 1939; Stern *et al.* 2001; Limtrakul *et al.* 2005). At the beginning of the experiment, the pressure drop caused the solid hydrate on the surface to begin decomposing. At this time, the phase change of the solid hydrate on the surface began. A dense water film gradually formed on the surface medium, which increased the compactness of the surface hydrate. In addition, this dense water film on the

periphery of the surface hydrate blocked the pressure conduction of the internal hydrate to a certain extent, thereby inhibiting hydrate decomposition (figure 2a). In the mid-stage, with the decomposition of solid hydrates, the surface temperature dropped rapidly and the water film on the surface gradually changed. A metastable ‘quasi-liquid film’ was formed (Takeya & Ripmeester 2008; Rehder *et al.* 2012), which could further maintain the phase equilibrium of the internal hydrate (figure 2b). In the later stage, the metastable ‘quasi-liquid film’ continued to grow inwards and formed a stable ‘quasi-liquid film’ that increased the mass transfer resistance of the hydrate and indirectly maintained the phase equilibrium of the internal hydrate (figure 2c). The steps showed that the hydrate’s self-protection effect during decomposition was the main reason for maintaining the hydrate’s internal phase equilibrium and inhibiting hydrate decomposition. Therefore, inhibiting the hydrate’s self-protection effect during decomposition and increasing the hydrate decomposition rate are the keys to this study.

3.2. The influence of a single electrolyte on the hydrate’s self-protection effect during decomposition

Thermodynamics, kinetics, heat transfer, mass transfer and the hydrate’s self-protection effect during decomposition all affect the kinetic process that interacts with multiple components and phases (Sohnel & Mullin 1988; Natarajan & Bishnoi 1994; Kashchiev 2000). Overall, the degree of disorder of the hydrate system determines the hydrate’s self-protection effect during decomposition.

3.2.1. *The influence of Na⁺ solution at different concentrations on the self-protection effect during decomposition.* This experiment contained five groups. The initial pressure was 8.80 MPa and the initial temperature was maintained at 2°C. According to the relationship diagram of the decomposition time of Na⁺ solutions with different concentrations and the pressure change (figure 3a), the following observations were made: the time for the Na2–Na5 curve to break through the self-protection effect was significantly shorter

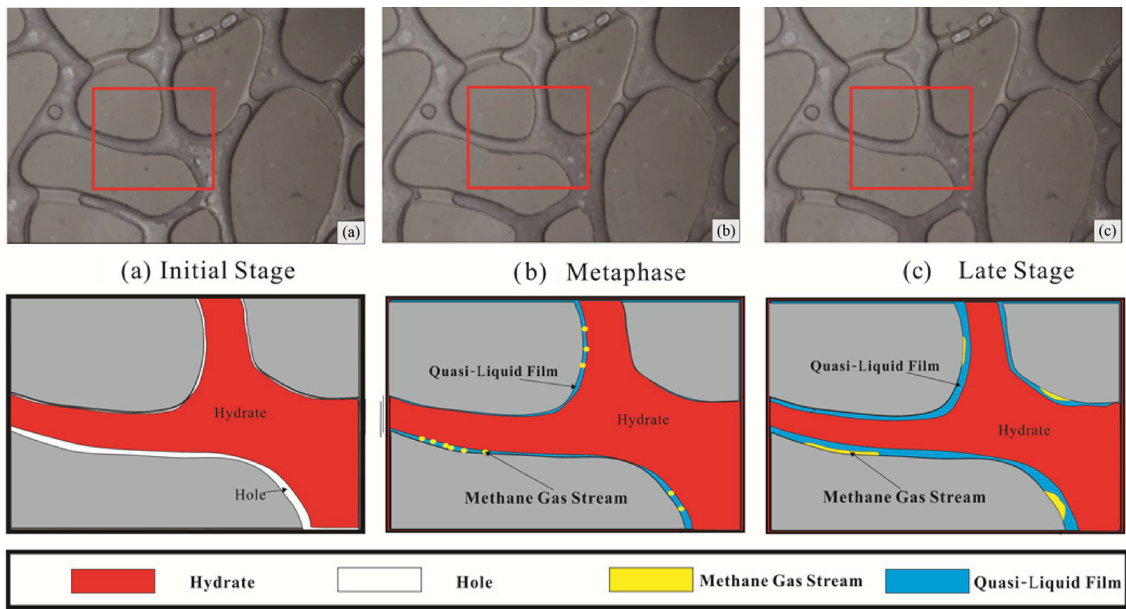


Figure 2. Schematic diagram of the hydrate decomposition process.

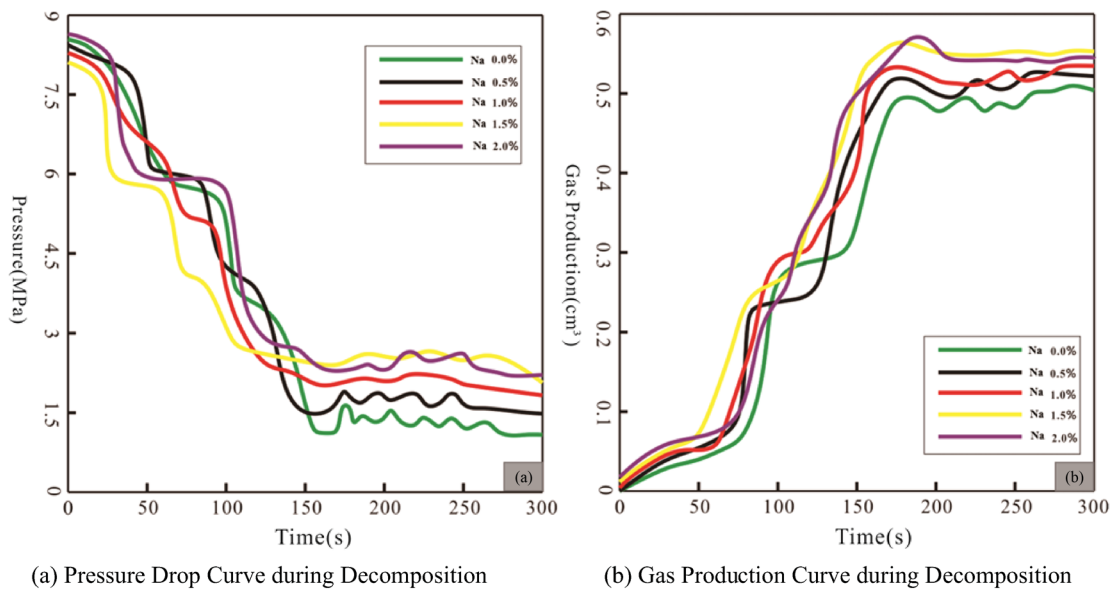


Figure 3. Variation curves of hydrate decomposition by depressurisation in different concentrations of Na⁺ solutions. (a) Pressure drop curve during decomposition. (b) Gas production curve during decomposition.

than that for the Na1 curve. Moreover, 50 s after the experiment started, the system pressures of the curves were 7.5, 7.0, 6.9, 5.8 and 5.5 MPa (Table 3). Comparing the variation trends of the Na2–Na5 and Na1 curves, it was found that when Na⁺ existed in the hydrate system, the mutation of the hydrate curve took a significantly shorter time to occur and the oscillation frequency in the later period was significantly reduced. These observations indicate that the presence of Na⁺ increases the degree of disorder of the hydrate system, changes the aggregation and dispersion behaviour of the free surface water and reduces the probability of free

Table 3. Parameters of natural gas hydrate decomposition in different concentrations of Na⁺ solutions

Curve no.	Concentration (%)	Time (s)	Temperature (K)	Pressure (MPa)	Gas production rate (cm ³ s ⁻¹)
S1	0	50	281.7	7.5	0.016
S2	0.5	50	277.6	7.0	0.021
S3	1.0	50	275.9	6.9	0.025
S4	1.5	50	275.7	5.8	0.029
S5	2.0	50	275.9	5.5	0.023

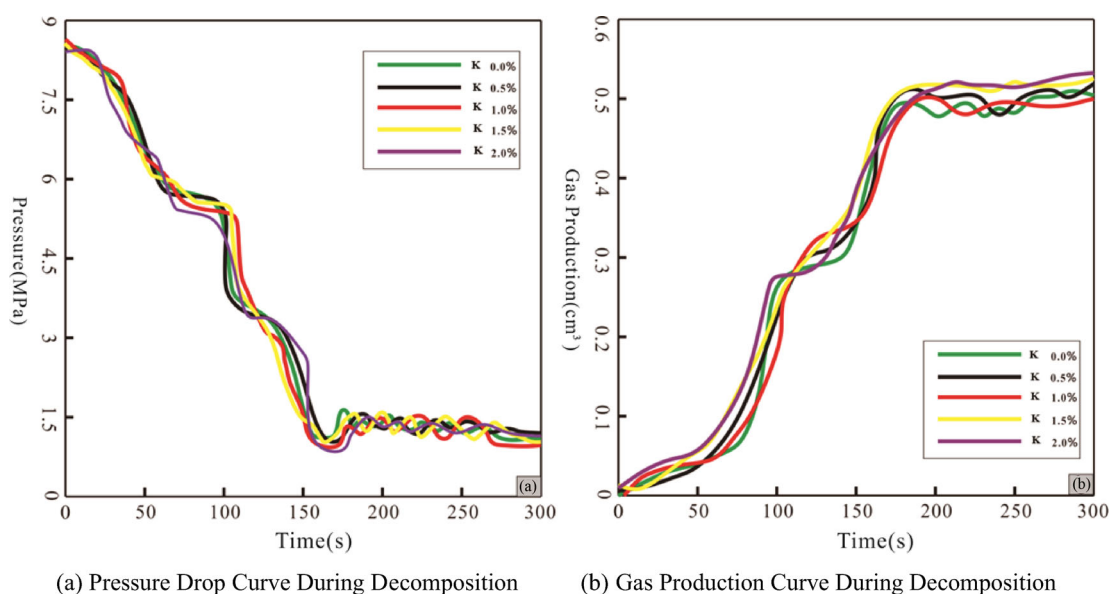


Figure 4. Variation curves of hydrate decomposition by depressurisation in different concentrations of K⁺ solutions. (a) Pressure drop curve during decomposition. (b) Gas production curve during decomposition.

water freezing, thereby inhibiting the occurrence of hydrate self-protection effect. Therefore, the mutation time of the Na2–Na5 curves was significantly shorter than that of the Na1 curve.

In addition, according to the time-varying trend of gas production with different Na⁺ concentrations (figure 3b), it can be observed that, except for the Na5 curve, the curves show a shortened mutation and an improved gas production rate as the Na⁺ concentration increases. The Na5 curve shows that with the increase in Na⁺ concentration, the gas production rate first increases and then decreases. These phenomena show that adding an appropriate concentration of Na⁺ ions to the hydrate system can inhibit the self-protection effect during decomposition. However, excessive concentrations also inhibit hydrate decomposition and reduce the decomposition rate. According to experimental data, at 50 s after the experiment started, the gas production rate of hydrates with different concentrations of Na⁺ ions were 0.016, 0.021, 0.025, 0.029 and 0.023 cm³ s⁻¹ (Table 3). From the change in the gas production rate within the same duration, it can be found that with an increase in the Na⁺ concentration in the hydrate, the gas production rate within the same duration first increased and then decreased. The maximum gas production rate occurred when the Na⁺ concentration was 1.5%. On the Na5 curve, the gas production rate decrease indicates that when the Na⁺ concentration in the hydrate was too high, although Na⁺ ions increased the degree of disorder in the hydrate system, it could also lead to the destruction of the ionization equilibrium of the system, thus changing the equilibrium constant of the hydrated ions and inhibiting the separation of methane molecules and the subsequent hydrate

decomposition. Consequently, the gas production rate was reduced.

To better understand the effect of Na⁺ ions on self-protection during hydrate decomposition, it is necessary to analyse its influencing mechanism. The degree of disorder is an essential factor that affects the phase equilibrium of the hydrate. When a large number of free moving electrolytes exist in the hydrate system, the activation performance of the hydrate system significantly improves and the degree of disorder in the gas–liquid–solid phase system significantly increases, which promotes extensive destruction of the hydrate cage structure, triggering the hydrate decomposition to occur earlier and accelerating the gas production efficiency. The degree of disorder in the hydrate system is similar to the entropy production change in electrochemistry; that is, matter always changes spontaneously to a high degree of disorder, namely from order to chaos (Ohmura *et al.* 2003; Zhao *et al.* 2015). When electrolytes exist in the hydrate system, the transition from order to disorder can be accelerated, thus inhibiting the self-protection effect and increasing the gas production rate.

3.2.2. The influence of K⁺ solution at different concentrations on the self-protection effect during decomposition. The K⁺ experiment has an experimental environment similar to that described previously. The experiment consisted of five groups. The initial pressure was 8.80 MPa and the initial temperature was maintained at 2°C. According to the relationship diagram of the decomposition time of Na⁺ solutions with different concentrations and the pressure change (figure 4a), the following facts were observed: five curves (K1–K5) have almost the same mutation time; 50 s after the hydrate

Table 4. Parameters of natural gas hydrate decomposition in different concentrations of K^+ solutions

Curve no.	Concentration (%)	Time (s)	Temperature (K)	Pressure (MPa)	Gas production rate ($\text{cm}^3 \text{s}^{-1}$)
S1	0	50	281.7	7.5	0.016
S2	0.5	50	276.8	7.4	0.016
S3	1.0	50	276.2	7.5	0.017
S4	1.5	50	275.9	7.6	0.018
S5	2.0	50	275.9	7.5	0.015

decomposition began, the system pressures of five curves were 7.5, 7.4, 7.5, 7.6 and 7.5 MPa, respectively (Table 4). Comparing the variation trends of the K1–K5 curves, it can be observed that when K^+ ions exist in the hydrate system, the mutation time of the hydrate curve is almost the same. The oscillation frequencies in the later period were also the same. These phenomena indicate that the existence of K^+ ions does not change the degree of disorder of the hydrate system. Therefore, K^+ ions cannot affect the self-protection effect during hydrate decomposition. Meanwhile, according to the changes in the gas production curve during hydrate decomposition (figure 4b), the final gas production curves of K4 and K5 show a clear rising trend, whereas the changes in K3 and K2 are almost the same as the K1 curve. This indicates that K^+ ions have little influence on the self-protection effect during hydrate decomposition. However, when the concentration of K^+ ions in the hydrate system is too high, it can also change the ionization equilibrium of the hydrate system, thus inhibiting hydrate decomposition. According to the experimental data, 50 s after the experiment began, the gas

production rates of hydrates with different concentrations of K^+ ions were 0.016, 0.016, 0.017, 0.018 and 0.015 $\text{cm}^3 \text{s}^{-1}$ (Table 3). It is clear that when the concentration of K^+ ions in the hydrate is below 2%, the effect of different K^+ concentrations on the hydrate gas production rate is weak. When the K^+ concentration in the hydrate was more than 2%, the gas production rate decreased slightly with an increase in K^+ concentration.

3.3. The influence of electrolytes in the synergistic system on self-protection effect

As mentioned previously, most electrolytes inhibit the self-protection effect during hydrate decomposition by changing the degree of disorder of the hydrate system, thus promoting hydrate decomposition. However, if the electrolyte concentration is too high, the ionization equilibrium of the hydrate system will be broken, resulting in an inhibition of the gas production rate (Maddah 2018; Bu et al. 2020; Wang et al. 2020). The research team mixed 0.1 mol of K^+ ions into each group of Na^+ -containing hydrate, aiming to explore the effect of the electrolyte in a synergistic system on the self-protection effect and gas production rate during hydrate decomposition.

To reduce the influence of the external environment on the experiment, the initial temperature and pressure of the synergistic system were the same as those used in the previous experiment. The concentrations of Na^+ ions in the synergistic system were 0, 0.5, 1, 1.5 and 2%. According to the relationship curve between the hydrate decomposition time and pressure change in the synergistic system with different concentrations (figure 5a), the mutation time from the S1 to

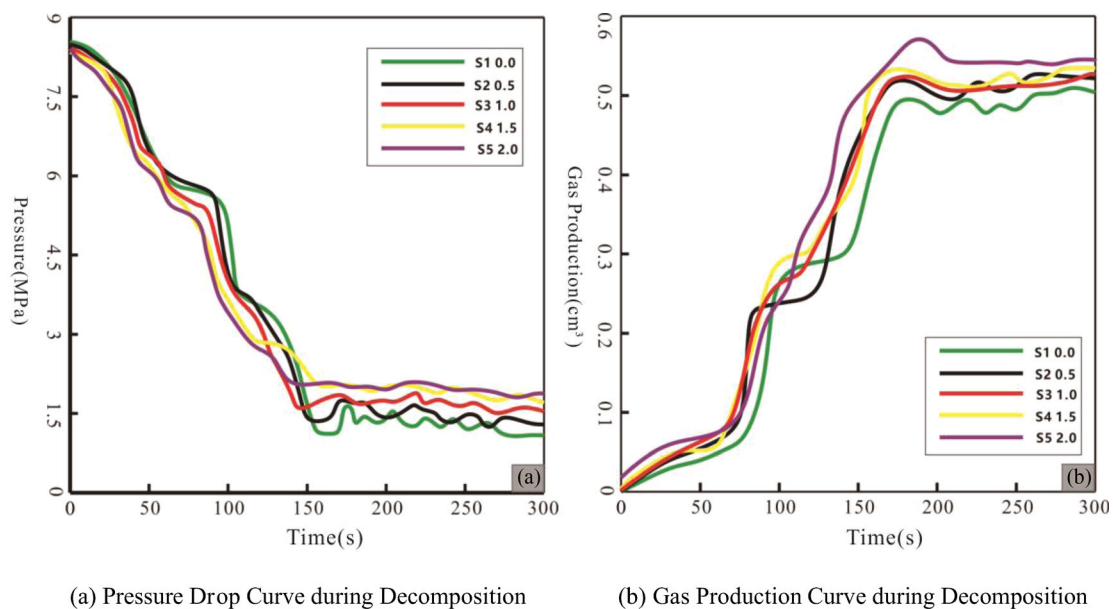
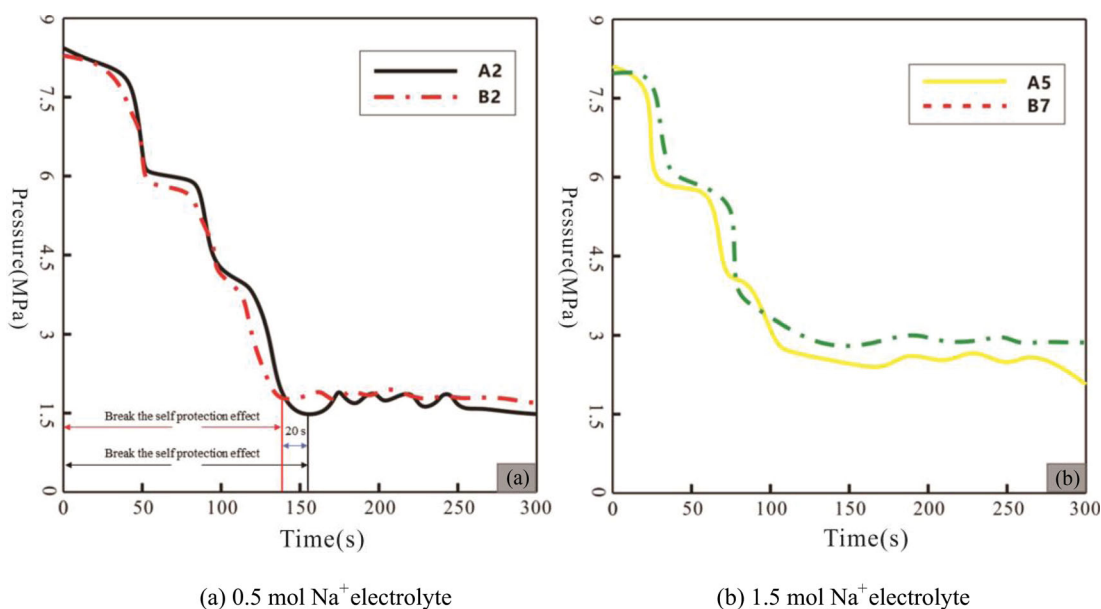


Figure 5. Variation curves of hydrate decomposition by depressurisation in the synergistic system with different concentrations. (a) Pressure drop curve during decomposition. (b) Gas production curve during decomposition.

Table 5. Parameters of hydrate decomposition in the synergetic system with different ion concentrations

Curve no.	Na ⁺ concentration (%)	K ⁺ concentration (%)	Time (s)	Temperature (K)	Pressure (MPa)	Gas production rate (cm ³ s ⁻¹)
S1	0	0	50	281.7	7.5	0.016
S2	0.5	0.1	50	279.3	7.3	0.023
S3	1.0	0.1	50	278.7	7.1	0.027
S4	1.5	0.1	50	276.7	6.9	0.031
S5	2.0	0.1	50	276.9	6.7	0.033

**Figure 6.** Comparison curve of pressure drop in the synergetic system with a single electrolyte: (a) 0.5 mol Na⁺ electrolyte and (b) 1.5 mol Na⁺ electrolyte.

S5 curve gradually shortened. Moreover, 50 s after the experiment began, the system pressures of each curve were 7.5, 7.3, 7.1, 6.9 and 6.7 MPa (Table 5). For instance, according to the trend of the pressure drop curves in the system with 0.5 and 1.5% Na⁺ solution (figure 6a and b), when both Na⁺ and K⁺ ions exist in the hydrate system, the time for the hydrate to break through the self-protective effect is significantly shorter than that for the hydrate system containing only Na⁺ ions, which is approximately 20 s. This indicates that the existence of K⁺ ions in the synergetic system can not only increase the degree of disorder of the hydrate system, but also enhance the Na⁺ ion's role in reducing the hydrate self-protection effect. Therefore, the mutation time of the B2 curve was significantly shorter than that of the A2 curve, shortening the time to 15 s.

In addition, figure 5b also reflects the changes in the pressure drop and gas production during hydrate decomposition in the synergetic system. The S1–S5 curves show that as the ion concentration of the synergetic system increases, the mutation time shortens and the gas production increases. This indicates that mixing an appropriate concentration of K⁺ ions in the hydrate system containing Na⁺ ions can inhibit the reduction of gas production caused by excessive Na⁺ con-

centration. According to the experimental data, 50 s after the experiment started, the gas production rate in the synergetic system was 0.016, 0.023, 0.027, 0.031 and 0.033 cm³ s⁻¹ (Table 5). It can be observed from the change in the gas production rate that with the increase in the ion concentration of the synergetic system, the gas production rate shows a continuously increasing trend. The maximum gas production rate was 0.33 cm³ s⁻¹ when the concentration of the synergetic system was 2.1%, which was 0.15 cm³ s⁻¹ higher than that of the single system. This shows that when K⁺ ions of an appropriate concentration are mixed into the hydrate system containing Na⁺ ions, the existence of K⁺ ions can occur in two ways: when the system has a low ion concentration, K⁺ ions can accelerate the disorders of the system, and when the system has a high ion concentration, K⁺ ions can reduce the activity of Na⁺ ions through the coexistence of ions, thereby increasing the gas production rate.

4. Synergetic system and hydrate decomposition mechanism

The synergetic system of Na⁺ and K⁺ ions was significantly better than the single electrolyte system in inhibiting the

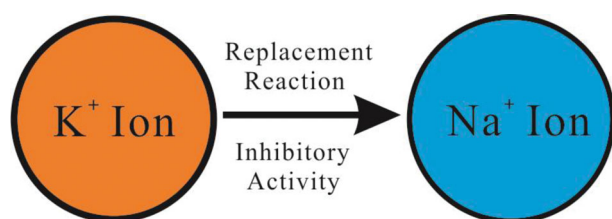


Figure 7. Diagram of the different electrolytes' replacement reactions.

hydrate's self-protection effect and increasing the gas production rate. The reasons are as follows: first, the synergistic system made it easier to change the degree of hydrate disorder compared to a single electrolyte. The coexistence of Na^+ and K^+ ions further increased the degree of disorder of the hydrate system, thereby changing the aggregation and dispersal behaviour of the free surface water, reducing the probability of free water freezing, thereby inhibiting the occurrence of hydrate self-protection effect (Lv et al. 2018; Zhang et al. 2018; Song et al. 2009; Liu 2018). At the same time, the existence of K^+ ions reversibly triggered the precipitation of Na^+ ions (figure 7). Therefore, within the system, the suppression of the replacement reaction between Na^+ and K^+ ions consumed part of the energy for the hydrate's self-protection effect, thereby indirectly inhibiting the self-protection effect. Second, when the Na^+ ion concentration in a single electrolyte system was too high, it destroyed the ionization equilibrium of the hydrate system and changed the equilibrium constant of the hydrated ions, thereby inhibiting the separation of methane molecules and subsequent hydrate decomposition (Ebeling 1969; Rouse 1992; Arkhipov et al. 2005). Consequently, the gas production slowed down. However, K^+ ions in the synergistic system can inhibit the activity of Na^+ ions, so the existence of K^+ ions can indirectly promote the gas production rate. This also shows that the synergistic system of Na^+ and K^+ ions has a better effect on inhibiting the self-protection of hydrate decomposition and increasing the gas production rate (Wu et al. 2018).

5. Conclusion

This study uses different types and different concentrations of electrolytes as inducers, exploring the influence of Na^+ and K^+ ions and their synergistic system on the self-protection effect of gas hydrate during its decomposition. According to the experimental results and parameters, including the pressure drop curve, gas production rate and gas production, the conclusions are as follows:

- (1) Electrolytes can inhibit the self-protection effect during hydrate decomposition. Na^+ ions have an inhibitory influence on the self-protection effect, while K^+ ions do not have a significant impact on the hydrate self-protection effect.

- (2) There was a negative correlation between the hydrate self-protection effect and Na^+ concentration. As the Na^+ concentration increased, the self-protection effect gradually weakened. However, an excessive Na^+ concentration can inhibit the hydrate gas production rate. The experiment found that when the Na^+ concentration was approximately 1.5%, it could effectively inhibit the self-protection effect during hydrate decomposition and prevent the reduction of the gas production rate.
- (3) The synergistic system of Na^+ and K^+ ions has a more significant inhibitory effect on the hydrate's self-protection effect than a single Na^+ ion solution. The synergistic system does not inhibit the hydrate gas production rate as its concentration increases.
- (4) The decomposition rate of hydrate containing single Na^+ ion or K^+ ion is $0.18 \text{ cm}^3 \text{ s}^{-1}$, whereas the decomposition rate of hydrate containing synergistic system electrolyte is as high as $0.33 \text{ cm}^3 \text{ s}^{-1}$. Therefore, a synergistic system with the same concentration can double the decomposition rate of hydrate compared with a single system.

Acknowledgements

The authors are grateful for the CNOOC Key Research and Development Projects (grant nos. CCL2019ZJFN1113, CCL2019ZJFN1114 and CCL2020ZJFN0314) and the National Natural Science Foundation of China (grant no. 52004220).

Conflict of Interest Statement

None declared.

References

- Arkhipov, Y.V., Baimbetov, F.B. & Davletov, A.E., 2005. Ionization equilibrium and equation of state of partially ionized hydrogen plasmas: pseudopotential approach in chemical picture, *Physics of Plasmas*, **12**, <https://doi.org/10.1063/1.1993062>.
- Bu, Y., Du, W., Du, J., Zhou, A., Lu, C., Liu, H. & Guo, S., 2020. The potential utilization of lecithin as natural gas hydrate decomposition inhibitor in oil well cement at low temperatures, *Construction and Building Materials*, <http://www.ncbi.nlm.nih.gov/pubmed/121274>
- Ebeling, W., 1969. Coulomb interaction and ionization equilibrium in partially ionized plasmas, *Physica*, **43**, 293–306, doi:10.1016/0031-8914(69)90009-3.
- Ebinuma, T., Oyama, H., Utiumi, T., Nagao, J. & Narita, H., 2008. Direct observation of characteristic dissociation behaviors of hydrate-bearing cores by rapid-scanning X-ray CT imaging, Proceedings of the 6th International Conference on Gas Hydrates.
- Egeberg, K. & Dickens, G.R., 1999. Thermodynamic and pore water halogen constraints on gas hydrate distribution at ODP Site 997 (Blake Ridge), *Chemical Geology*, **153**, 53–79.
- Gudmundsson, J.S., 1990. Method and equipment for production of gas hydrates, *Norwegian Patent*, 172080, 135.
- Guo, G.J., Li, M., Zhang, Y.G. & Wu, C.H., 2009. Why can water cages adsorb aqueous methane? A potential of mean force calculation on

- hydrate nucleation mechanisms, *Physical Chemistry Chemical Physics*, **11**, 10427–10437.
- Handa, Y.P., 1986. Calorimetric determinations of the compositions, enthalpies of dissociation, and heat capacities in the range 85 to 270 K for clathrate hydrates of xenon and krypton, *The Journal of Chemical Thermodynamics*, **18**, 891–902.
- Kamath, V.A. & Godbole, S.P., 1987. Evaluation of hot-brine stimulation technique for gas production from natural gas hydrates, *Journal of Petroleum Technology*, **39**, 1–379.
- Kashchiev, D., 2000. *Nucleation*. Elsevier.
- Li, S.X., Zhang, M.Q. & Li, J., 2012. Experimental investigation of hot-brine injection to dissociate natural gas hydrate at different hydrate saturation, *Journal of Experimental Mechanics*, 04.
- Li, Z.D., Tian, X., Li, Z., Xu, J.Z., Zhang, H.X. & Wang, D.J. 2020. Experimental study on growth characteristics of pore-scale methane hydrate, *Energy Reports*, **6**, 933–943.
- Limtrakul, S., Rojanamatin, S., Vatanatham, T. & Ramachandran, A., 2005. Gas-lift reactor for hydrogen sulfide removal, *Industrial & Engineering Chemistry Research*, **44**, 6115–6122.
- Liu, W.Y., 2018. Experimental study on the effect of salts on the stability of methane hydrate. China University of Petroleum.
- Luo, C.X., 2013. Research and development status of methane hydrate in the world, *Petroleum & Petrochemical Material Procurement*, **21**(12), 16–23.
- Lv, Q., Zang, X., Li, X. & Li, G., 2018. Effect of seawater ions on cyclopentane-methane hydrate phase equilibrium, *Fluid Phase Equilibria*, **458**, 272–277 doi:10.1016/j.fluid.2017.11.031.
- Maddah, M., Maddah, M. & Peyvandi, K., 2018. Molecular dynamics simulation of methane hydrate formation in presence and absence of amino acid inhibitors, *Journal of Molecular Liquids*, **269**, 721–732.
- Milkov, A.V., 2004. Global estimates of hydrate-bound gas in marine sediments: how much is really out there?, *Earth-Science Reviews*, **66**, 183–197.
- Nagao, J., Shimomura, N., Ebinuma, T. & Narita, H., 2008. Observation of ice sheet formation on methane and ethane gas hydrates using a scanning confocal microscopy.
- Natarajan, V., Bishnoi, P.R. & Kalogerakis, N., 1994. Induction phenomena in gas hydrate nucleation, *Chemical Engineering Science*, **49**, 2075–2087.
- Ohmura, R., Ogawa, M., Yasuoka, K. & Mori, Y.H., 2003. Statistical study of clathrate-hydrate nucleation in a water/hydrochlorofluorocarbon system: Search for the nature of the “memory effect”, *The Journal of Physical Chemistry B*, **107**, 5289–5293.
- Rehder, G. et al., 2012. Methane hydrate pellet transport using the self-preservation effect: a techno-economic analysis, *Energies*, **5**, 2499–2523.
- Rouse, C.A., 1992. Ionization equilibrium equation of state. *Astrophysical Journal* **135**.
- Sloan, E.D., Jr. & Koh, C.A., 2007. *Clathrate Hydrates Of Natural Gases*. CRC press
- Sohnel, O. & Mullin, J.W., 1988. Interpretation of crystallization induction periods[J]. *Journal of Colloid and Interface Science*, **123**(1), 43–50.
- Song, Y.C., Yang, M.J. & Liu, Y. et al., 2009. Effect of ions on phase equilibrium of methane hydrate[J]. *Journal of Chemical Industry and Engineering*, **60**, 1362–1366.
- Stern, L.A., Circone, S., Kirby, S.H. & Durham, W.B., 2001. Anomalous preservation of pure methane hydrate at 1 atm, *The Journal of Physical Chemistry B*, **105**, 1756–1762.
- Takeya, S., Ebinuma, T., Uchida, T., Nagao, J. & Narita, H., 2002. Self-preservation effect and dissociation rates of CH₄ hydrate, *Journal of Crystal Growth*, **237**, 379–382.
- Takeya, S. & Ripmeester, J.A., 2008. Dissociation behavior of clathrate hydrates to ice and dependence on guest molecules, *Angewandte Chemie International Edition*, **47**, 1276–1279.
- Tang, L.G., Xiao, R., Li, G., Feng, Z.P., Li, X.S. & Fan, S.S., 2006. Experimental investigation of production behavior of gas hydrate under thermal simulation, *Chinese Journal of Process Engineering*, **6**, 548.
- Uchida, T., Sakurai, T. & Hondoh, T., 2011. Ice-shielding models for self-preservation of gas hydrates, *Journal of Chemistry and Chemical Engineering*, **5**, 691–705.
- Volmer, M., 1939. *Kinetik der phasenbildung*.
- Wang, Z., Sun, B. & Gao, Y., 2020. Formation and decomposition of natural gas hydrate, In: Wang Z., *Natural Gas Hydrate Management in Deepwater Gas Well* (pp. 9–50). Springer, Singapore.
- Wu, Z., Li, Y., Sun, X., Wu, P. & Zheng, J., 2018. Experimental study on the effect of methane hydrate decomposition on gas phase permeability of clayey sediments, *Applied Energy*, **230**, 1304–1310.
- Yakushev, V.S., 1989. Gas hydrates in cryolithozone, *Soviet Geology and Geophysics*, **1**, 100–105.
- Yang, M.J. & Liu, Y., 2009. Effects of porous media and salinity on phase equilibrium of methane hydrates, *Journal of Dalian University of Technology*, **51**, 31–35 (in Chinese).
- Xuan, Z.Q., Li, Z.M. & Wu, B.H. et al., 2018. Brief introduction of new energy sources of natural gas hydrate—a summary of the current situation of global trial production, development and research of natural gas hydrate[J], *Geology of Chemical Minerals*, **40**(1), 48–52.
- Zhang, B. et al., 2018. Methane hydrate formation in mixed-size porous media with gas circulation: effects of sediment properties on gas consumption, hydrate saturation and rate constant, *Fuel*, **233**, 94–102.
- Zhao, J. et al., 2015. Existence of a memory effect between hydrates with different structures (I, II, and H), *Journal of Natural Gas Science and Engineering*, **26**, 330–335.