

# New Anti-agglomerants : Effect of Coconut Oil Amide Propyl Betaine on Hydrate Agglomeration

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## Abstract

The purpose of this work is to explore the effect of new anti-aggregation agent ( coconut oil amide propyl betaine ) on the flow stability of oil-water emulsion system under different water content and flow rate conditions, and confirm that the new anti-aggregation agent under high water content and even pure water conditions can still play an anti-coagulation role, so that hydrates can form stable and mobile mud. In addition, in order to explore the parameter changes in the system caused by the transient changes ( shutdown and start ) in the flow system and the flow characteristics of hydrate in the non-flat pipeline, the flow characteristics of hydrate slurry with inclined pipe section are explored, and the changes in the flow characteristics of hydrate with shutdown and restart in the actual production process are explored by stopping and restarting the equipment.

New Anti-agglomerants : Effect of Coconut Oil Amide Propyl Betaine on Hydrate Agglomeration in Pipeline Transportation System

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## Summary

As a good low-dose hydrate inhibitor, the anti-agglomeration agent can keep the generated hydrate particles well dispersed, and avoid the plugging caused by a large amount of hydrate aggregation. However, the application of most Anti-agglomerants is severely limited by the moisture content in the system, that is, they cannot play a role under high moisture content. The purpose of this work is to explore the effect of new anti-aggregation agent ( coconut oil amide propyl betaine ) on the flow stability of oil-water emulsion system under different water content and flow rate conditions, and confirm that the new anti-aggregation agent under high water content and even pure water conditions can still play an anti-coagulation role, so that hydrates can form stable and mobile mud. In addition, in order to explore the parameter changes in the system caused by the transient changes ( shutdown and start ) in the flow system and the flow characteristics of hydrate in the non-flat pipeline, the flow characteristics of hydrate slurry with inclined pipe section are

explored, and the changes in the flow characteristics of hydrate with shutdown and restart in the actual production process are explored by stopping and restarting the equipment. The conclusion can provide theoretical support for hydrate anti-agglomeration in high water content system and hydrate slurry flow in unconventional pipe closure and restart system.

## Introduction

Natural gas hydrate, also known as methane hydrate, is a solid compound with ice-like appearance but different crystal structures formed by natural gas and water in a non-stoichiometric (Baek et al. 2017; Dong et al. 2020; Wu et al. 2021). In 1934, Hammerschmid et al. found that hydrate was one of the reasons for blockage of natural gas pipeline mining equipment, and its formation temperature was far above ice. The initial stage of natural gas exploitation usually has a high moisture content. The full contact of air flow and free water in the pipe provides a large number of nucleation sites, and hydrates are formed in the pipe when the temperature and pressure conditions are appropriate. In recent years, with the gradual transfer of oil and gas exploitation from inland to deep sea areas, the possibility of hydrate formation is further enlarged under the environment of high pressure and low temperature, and the possibility of hydrate accumulation and pipe blockage is also increased. Once the gas well is stopped or the pipeline is blocked, the transportation accident is caused, which is easy to cause equipment damage and large economic losses, and even cause casualties. In the past 10 years, hydrate has become an important issue in the field of flow security. Controlling the risk of hydrate formation and blockage in pipelines and ensuring the safety of deep-sea oil and gas flow have become an urgent problem for researchers in various countries.

In the past, some engineering methods that were ineffective or costly were often used to prevent or inhibit the formation of hydrates, such as dehydration and adding thermodynamic inhibitors. In order to save the economic cost of natural gas hydrate risk management and improve engineering efficiency, low-dose hydrate inhibitors ( kinetic inhibitors and anticoagulants ) have been found and widely used in hydrate blockage prevention and control. Kinetic inhibitors are usually water-soluble polymers, and the existence of hundreds of ppm kinetic inhibitors can change the intrinsic kinetic characteristics of hydrate growth, prolong the induction period required for nucleation, so that the fluid can flow smoothly in a certain time. However, the application of kinetic inhibitors is affected by the environment. When the undercooling is too high, kinetic inhibitors will lose their effectiveness. Therefore, scholars have developed compound inhibitors of various kinetic inhibitors and synergistic agents to avoid this shortcoming.

On the contrary, the inhibitor is not involved in the nucleation and growth of hydrate, so it can play a role at high undercooling. AA can keep the generated hydrate particles in good dispersion, and avoid the plugging caused by a large amount of hydrate accumulation. Therefore AA usually plays a role in the management and control of hydrate particles. Quaternized ammonium salt ( QAS ) is the most common Anti-agglomerants. Quaternized ammonium salt ( QAS ) with many commercial applications has been used for hydrate Anti-agglomerants, and it has been proved that it can withstand high undercooling. The single-tailed quaternary ammonium salt QAS contains a hydrophobic tail group of 10 – 14 carbon atoms with ammonium head groups and anions . Due to the higher enthalpy of the hydrophilic group of the inhibitor, the hydrogen bond formed between the hydrate and AA is more solid. Therefore, anti-aggregation in oil-water coexistence system will make oil-water phase emulsification, resulting in water phase dispersed in the oil phase in the form of water droplets. Gas hydrates formed on the surface of water droplets will be solubilized in the microemulsion and thus difficult to aggregate. Because of this, the application of most Anti-agglomerants is severely limited by the moisture content in the system, that is, they cannot play a role under high moisture content. In addition, QAS has limitations such as toxicity and low biodegradability.

However, scholars have never stopped their research and development on the applicability of Anti-agglomerants agents in different systems and new green Anti-agglomerants agents. Sun et al. (Sun et al. 2013) developed a new low-dose surfactant ( 0.2 wt. % ) and found that it can play an anti-coagulation role in any water content system, even in pure water systems without oil-in-water emulsions. Based on the experimental results, they obtained a new anti-coagulation mechanism of emulsion-free hydrates based on micelle equilibrium. Phan et al. (Phan et al. 2021) aimed to accurately predict and design the molecular

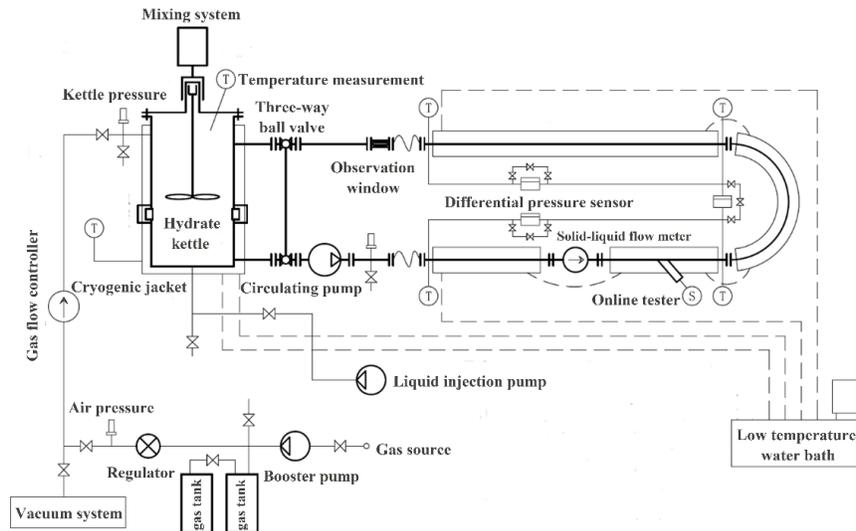
structure and properties of the Anti-agglomerants agent by simulation method. They compared the kinetic simulation data with the experimental data of micromechanical force measurement and obtained good consistency. The results showed that the entropy and solvent free energy of AA and its molecular orientation at the rehydrate-oil interface greatly determined the Anti-agglomerants performance of AA. Gao et al. (Gao et al. 2009) found through experiments that the increase of salt concentration of brine in the high water content system would make the performance of the polymer inhibitor step-by-step increase. Firoozabadi et al. (Firoozabadi et al. 2014) found that in the system containing carbon dioxide and other acidic components, the Anti-agglomerants agent will lose its original effect. By adding a small amount of sodium hydroxide and eliminating foaming oil, good synergistic benefits can be achieved. Zhao et al. (Zhao et al. 2016) found that the addition of lithium hydroxide was more effective than the traditional sodium hydroxide for the Anti-agglomerants, and the dosage was greatly reduced. They suggested that there was a complex synergy between sodium chloride and AA, and an increase in salt concentration would significantly reduce the use of basic chemicals. Li et al. (Li et al. 2018) studied the anti-agglomeration performance of different concentrations of Anti-agglomerants on cyclopentane hydrate through micromechanical force measurement device, and proposed the mechanism of Anti-agglomerants on hydrate at different concentrations. Dong et al. (Dong et al. 2018) reported the effect of water content and sodium chloride concentration on the effectiveness of AA in the presence of cosurfactant ( span80 ). The results showed that sodium chloride decreased the anti-aggregation effect of the compound system when the water content was 10 %, while it was promoted when the water content was 20 – 30 %. NaCl had no significant effect on AA performance at 50 % moisture content. In the case of 80 – 100 % moisture content, the water-in-oil emulsion with hydrate as continuous phase needs higher salt concentration to promote anti-agglomeration.

At present, the research on the hydrate management strategy for steady flow has gradually matured, but the research on the transient situation ( shut-down and start-up ) in the flow system is very scarce. During the shut-in period, the temperature is rapidly cooled due to the static fluid, so the environment may reach the hydrate formation conditions during this period. When restarted, due to the sudden increase in the flow rate, the full mixing of oil, gas and water leads to the increase of the nucleation site of the hydrate, which may lead to the explosive growth of the hydrate and cause plugging. The shutdown caused by various factors in practice is uncontrollable, which is the most worrying and important threat to hydrate formation. Therefore, it is urgent to explore hydrate formation and flow characteristics under shutdown and restart conditions. Some studies have been devoted to the flow characteristics of transient hydrate slurry and the influence of rheological properties and Anti-agglomerants on the plugging characteristics of hydrate during restart (Zhang et al. 2021; Kakitani et al. 2019; Kakitani et al. 2022; Shuard et al. 2017; Sohn et al. 2017). Shi et al. (Shi et al. 2018) carried out a series of experiments on the shutdown and restart of carbon dioxide hydrate in water-dominated system. The results show that the sudden restart after the first shutdown will lead to explosive hydrate formation and irreversible blockage. Liu et al. (Liu et al. 2021) explored the visualized high-pressure flow loop to explore the plugging characteristics of hydrate shut-down and restart. The results showed that shut-down and restart would lead to continuous decrease of system temperature and acceleration of hydrate accumulation. With the extension of shut-down time, the plugging risk of hydrate was further increased, and low liquid loading would accelerate the deposition process of hydrate. Yan et al. (Yan et al. 2014) carried out a long-term shutdown test ( 2 hours, 4 hours, 8 hours ) in restart under the action of AA can be safe flow, shutdown restart experiments show that hydrate slurry has obvious shear thinning behavior.

The purpose of this work is to explore the effect of new anti-aggregation agent ( coconut oil amide propyl betaine ) on the flow stability of oil-water emulsion system under different water content and flow rate conditions, and confirm that the new anti-aggregation agent under high water content and even pure water conditions can still play an anti-coagulation role, so that hydrates can form stable and mobile mud. The flow characteristics of hydrate slurry with inclined pipe section were explored, and the change of flow characteristics of hydrate with shutdown and restart in the actual production process was explored by stopping and restarting the equipment. The conclusion can provide theoretical support for hydrate anti-agglomeration in high water content system and hydrate slurry flow in unconventional pipe closure and restart system.

## 2. Experimental materials and procedures

Experimental device : The detailed information of the self-made hydrate flow loop experimental device has been reported in previous literature. In short, the system consists of an intake system, a liquid intake system, a cooling system and a data acquisition system. Piston metering pump ( 30L / h; 50MPa ) can be pumped into the hydrate kettle, circulating pump ( 1400rpm ; 50 Hz ) can be used to drive the fluid in the kettle into the loop and make the liquid flowing into the loop circulate. The total length of the loop test section is 30 m, the inner diameter is 22 mm, the total volume is 45 L, and the design pressure of the pipeline is 16 MPa. The whole test section and the hydrate kettle are wrapped by the cooling jacket. The coolant pumped by the cooling system can cool the loop, and the temperature control range is - 10 - 40 °C. In addition, pressure sensors, differential pressure sensors, temperature sensors, gas mass flowmeters, liquid mass flowmeters, focused beam reflection measurement ( FBRM ) and particle video microscope ( PVM ) are equipped to detect the temperature and pressure state of fluid in the loop and the macroscopic and microscopic flow characteristics. **Fig. 1** is the experimental device diagram.



**Fig. 1. Experimental device diagram**

Experimental procedure :

Open the vacuum pump and empty the entire experimental loop to 0.08 MPa to remove air from the tube. Observe whether the pressure gauge changes, check the air tightness of the experimental circuit. Pump a predetermined amount of tap water or coconut oil amide propyl betaine solution into the hydrate kettle. Start magnetic centrifugal pump stirring evenly, at the same time, start water bath and set the experimental inlet temperature  $T_0$ . Adjust the angle between the loop experimental section and the horizontal plane, open the circulating pump on the loop, and the liquid in the kettle enters the loop and circulates at a certain flow rate. Open carbon dioxide cylinders and piping intake valves and pressure regulating valves. When the pressure in the pipeline reaches the experimental pressure and reaches the dissolution equilibrium ( the pressure remains unchanged within 30 min ), the gas injection process is stopped. Also ensure that the temperature in this step is higher than the phase equilibrium temperature of carbon dioxide hydrate. FBRM and PVM were started to record the change of particle size before and after hydrate formation. Get the string length distribution of particles and the microscopic image of the experimental system ; the water bath temperature was set to a set value  $T_1$ , and the data acquisition system was started. At the same time, the macroscopic morphology of hydrate formation and flow was observed through the visual window. In the cooling process of some experimental schemes, the circulating pump was closed to simulate the shutdown

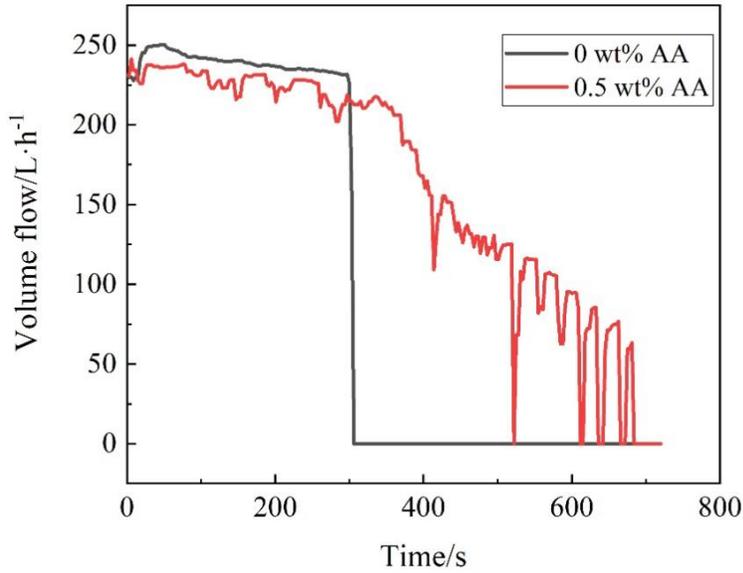
environment of the actual pipeline. When the temperature and pressure of the experimental system tend to be stable or the experiment reaches the preset duration or when the flow rate of the pipeline decreases to zero, the loop is blocked by the hydrate. Close the circulating pump and cooling system. Open the pipe drain valve to remove carbon dioxide and liquid from the pipe. Then reinjection clean water to flush the pipe and use compressed air to clean the pipe. Hydrate formation experiment ended, the next set of experiments.

### 3. Result and discussion

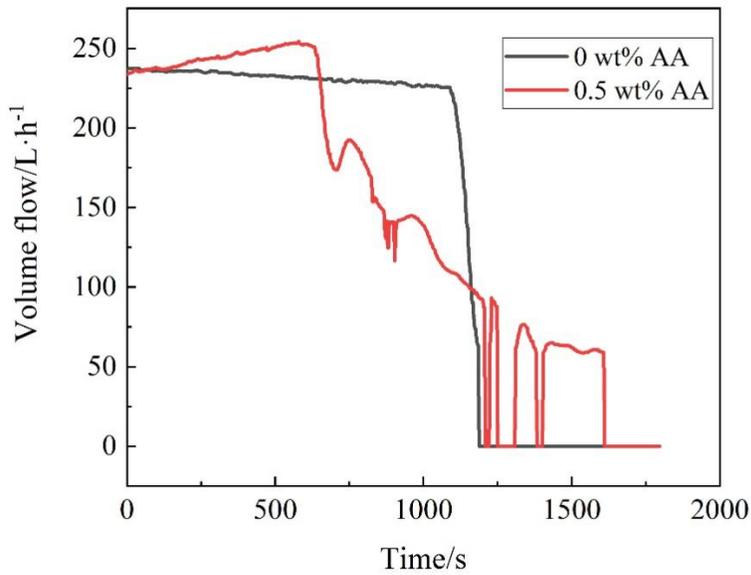
In this experiment, the influence of water content on the effect of polymer inhibitor(Composition of the oil phase is No. 10 industrial white oil), the influence of initial flow rate on the flow characteristics of hydrate slurry, the plugging characteristics of hydrate slurry in inclined pipe, and the plugging characteristics and mechanism of hydrate under the condition of shutdown and restart were explored. The initial pressure of each group was 3.2 MPa, and the initial temperature of each group was 12 °C. The initial flow of the power control system of the circulating pump was changed.

**3.1 Antipolymer effect under different moisture content.** Polymer inhibitors disperse hydrate particles in fluid and allow hydrate to be transported as mud. Some of the most effective and typical Anti-agglomerants agents are quaternary ammonium salts. Usually, they consist of ionic head groups and various hydrophobic tail groups. AA molecules are usually the most effective in the presence of a large number of hydrocarbon phases in the mixture, and in the so-called high water content state, the anti-agglomeration performance decreases ; therefore, it is very important to understand and improve the function of polymer inhibitor under different water content conditions.

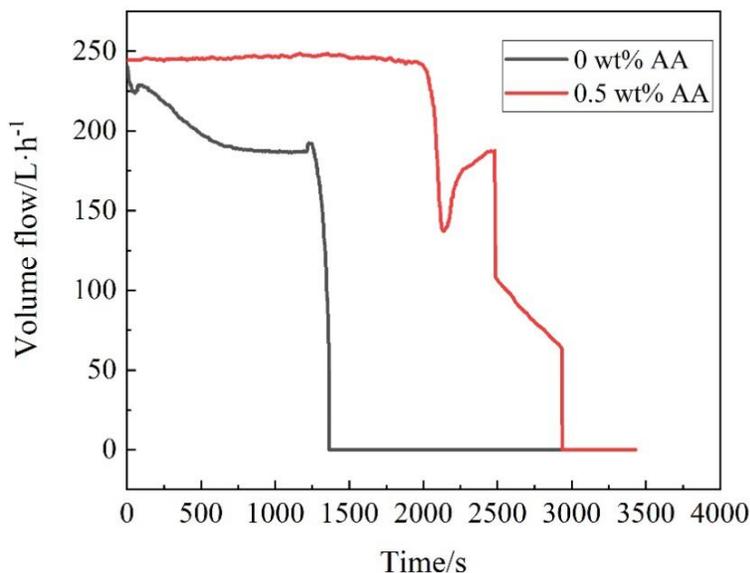
Firstly, the effect of polymer inhibitor on the flow of hydrate slurry under the condition of 50 % and 70 % water content was compared. Under the condition of 50 % water content, the plugging time of adding polymer inhibitor and without polymer inhibitor was 5.1 min and 11 min, respectively. Under the condition of 70 % water content, the plugging time of existing polymer inhibitor and without polymer inhibitor was 20 min and 27 min, respectively. Obviously, coconut oil amide propyl betaine can effectively play the role of anti-coagulation of hydrate in oil-water two-phase system and prolong the flow time of hydrate slurry. In addition, an increase in water content also leads to a decrease in gas solubility per unit volume of oil-water emulsions during nucleation and growth. Gas mass transfer limitation reduces the nucleation and growth rate of hydrate, which led to longer blockage time. In order to further study whether the new polymer inhibitor is limited by moisture content, the anti-coagulation effect of polymer inhibitor under pure water condition was studied. Under the condition of pure water, the plugging time of adding Anti-agglomerants and without Anti-agglomerants is 23 min and 49 min respectively. Obviously, the anti-coagulation effect of cocoamidopropyl betaine on hydrate particles is not limited to water content, even in pure water conditions, it can effectively enhance the fluidity of hydrate slurry and prolong the plugging time. In addition, with the increase of water content, the blocking time of the system is gradually prolonged. In the oil-water system, the solubility of gas near the hydrate formation region plays an important role in the nucleation and growth of hydrate. The increase of water content can significantly reduce the solubility of gas molecules in the emulsion system. **Figs 2, 3, 4** are flow curves of 50 %, 70 % and pure water, respectively.



**Fig. 2-Flow rate curves of hydrate slurry with and without Anti-agglomerants under the condition of 50 % moisture content**



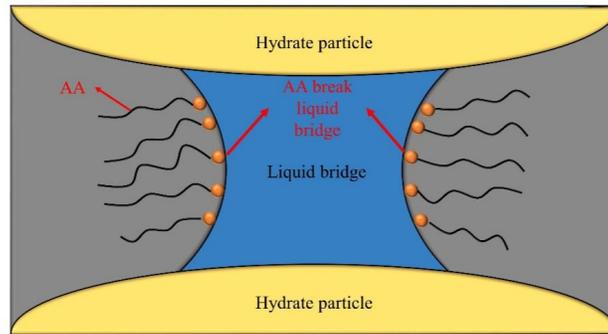
**Fig. 3-70 % water content curves of hydrate slurry flow with and without inhibitor**



**Fig. 4-Flow Curve of Hydrate Slurry with and without Antipolymer in Pure Water**

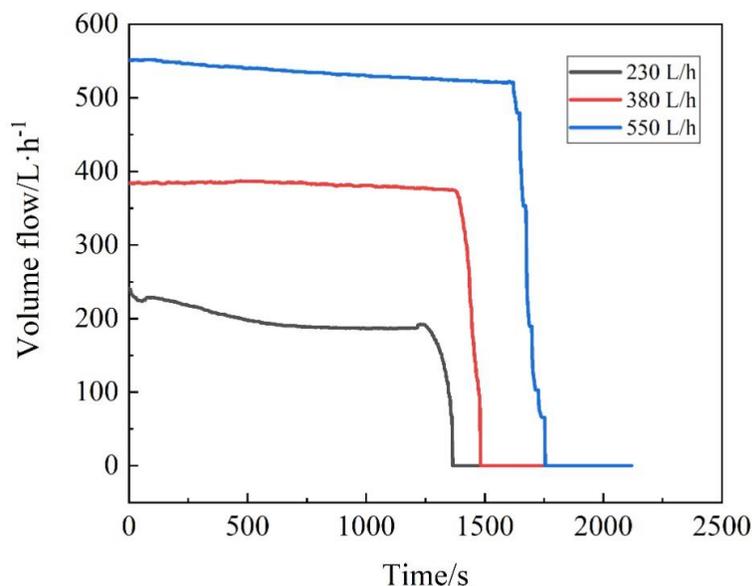
The experiments were carried out at the initial flow rate of 230 L / h under different moisture content. It can be seen from the curve that although the new Anti-agglomerants agent can effectively improve the fluidity of hydrate slurry under different moisture content and alleviate the trend of plugging, the flow change trend of the system with Anti-agglomerants agent is usually disordered. Under the conditions of 50 % and 70 % moisture content, many times of the flow rate of the system temporarily dropped to zero before the hydrate slurry completely stopped flowing. We suspect that when hydrate blockage occurs in the system with Anti-agglomerants agent. The anti-agglomeration agent can decompose the hydrates that have been generated, aggregated or deposited on the wall of the pipe to restore the flow of the system, and the change of the hydrate aggregation state will also make the flow of the system change irregularly. Therefore, the flow change trend shown in the following figure will appear.

Through previous studies, it can be known that the polymer inhibitor can change the dispersion state of water molecules in oil-water emulsion to make the emulsion more stable, resulting in water dispersed in the oil phase in the form of water droplets. Gas hydrates formed on the surface of water droplets will be solubilized in the microemulsion and thus difficult to aggregate. Therefore, the polymer inhibitor can play an anti-coagulation role of hydrate particles in oil-water emulsion system. In pure water system, the mechanism of anti-agglomeration effect of anti-agglomeration agent may be different from that of oil-water emulsion. We believe that the aggregation behavior of hydrate crystals is closely related to the cohesion between hydrate particles. Coconut amide has a long alkyl chain, which can provide a more dense barrier, thereby effectively reducing the cohesion between particles. These molecules can reduce the interfacial tension and increase the contact angle between natural gas hydrate and water, so as to minimize the interaction between natural gas hydrate particles. In addition, AA also affects the liquid bridge between gas hydrate particles by breaking water molecules, thereby destabilizing the cohesion between hydrate particles. **Fig. 5** shows the mechanism of hydrate Anti-agglomerants caused by Anti-agglomerants in self-made pure water system.



**Fig. 5-Schematic diagram of Anti-agglomerants affecting hydrate bridge in pure water system**

**3.2 Effect of initial flow rate on flow characteristics.** The flow curves of hydrate slurry under different initial flow rates in pure water system were showed in **Fig. 6** . The flow characteristics of hydrate slurry under the initial flow rates of 230 L / h, 380 L / h and 550 L / h were investigated. The stable flow time of hydrate slurry was 23 min, 25 min and 30 min, respectively. Obviously, increasing the initial flow rate can significantly prolong the plugging time of hydrate slurry. From the perspective of hydrate nucleation, this may be due to the inhibition or delay of hydrate nucleation caused by high shear, which makes it difficult to reach the critical size required for hydrate formation. Moreover, high flow rate increases the flow friction ( heat generated ), weakens the cooling effect of temperature control system, inhibits the nucleation and growth of hydrate in the pipeline transportation system, and thus prolongs the induction period of hydrate. From the perspective of hydrate plugging mechanism, high-velocity fluid can not only destroy the formed hydrate polymer, but also reduce the probability of coalescence between hydrate particles, which greatly reduces the risk of plugging. Excessive flow velocity also increases the wall shear rate, making it difficult for hydrate particles to adhere to the wall. Hydrate deposition on the wall surface can reduce the flow area of slurry, so the flow shear rate of the deposition surface increases rapidly during hydrate deposition. When the surface flow shear rate reaches the critical point, the sediment will begin to fall off.



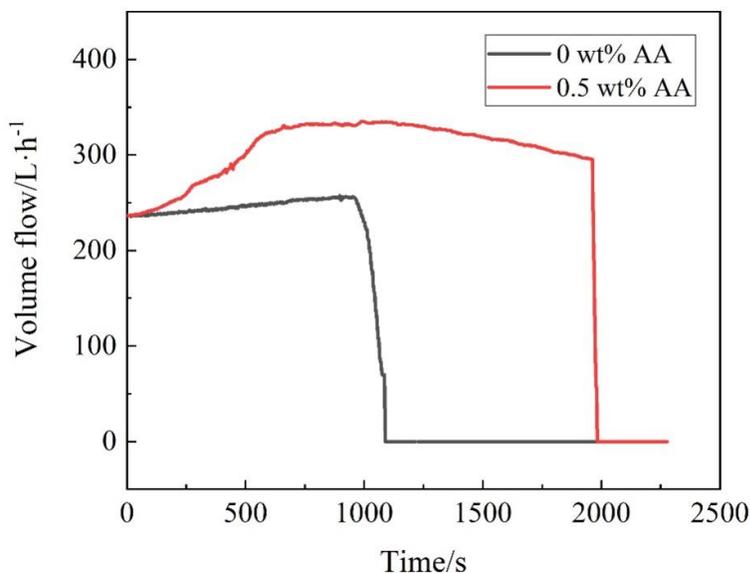
**Fig .6-Flow curves of hydrate slurry under different initial flow rates in pure water system**

From the experimental results, no matter from the aspects of hydrate nucleation or plugging mechanism, increasing the flow rate can effectively reduce the risk of plugging. This is also in line with the research conclusions of most scholars (Liu et al. 2021; Zhang et al. 2021; Shi et al. 2018; Zhang et al. 2022). However, although the high shear effect brought by high flow rate and the weakening of cooling effect will limit or inhibit the nucleation growth and aggregation deposition of hydrate under certain conditions, higher flow rate will also provide more nucleation sites, accelerate the interface disturbance and increase the gas-liquid contact area. Accelerating the induction period of hydrates increases the risk of plugging. Therefore, the influence of different initial flow rates under different systems on the flow characteristics of hydrate slurry should be further studied. If the trend of hydrate plugging can be affected by controlling the flow rate, the economic cost of hydrate plugging prevention will be greatly reduced compared with adding chemical additives. Therefore, it is of great practical significance to explore the influence of flow rate on the flow characteristics in the pipeline system for hydrate prevention and control strategy.

**3.3 Flow characteristics of hydrate slurry under inclined tube conditions.** The actual operation conditions of oil and gas gathering and transportation pipelines are complex. The change of morphology and position of pipeline flow area and the change of pipeline operation conditions will affect the plugging process of hydrate. The flow characteristics of hydrate slurry under various pipeline structures and operation conditions are still unclear. Therefore, the flow and plugging characteristics of hydrate slurry under special conditions of pipeline still need further study. Due to the complexity of natural gas transportation pipeline laying environment and the need of conditions, there are usually parts laid on the slope to form inclined pipelines. The study of hydrate formation and flow characteristics in the slope is of great significance for the prevention of blockage.

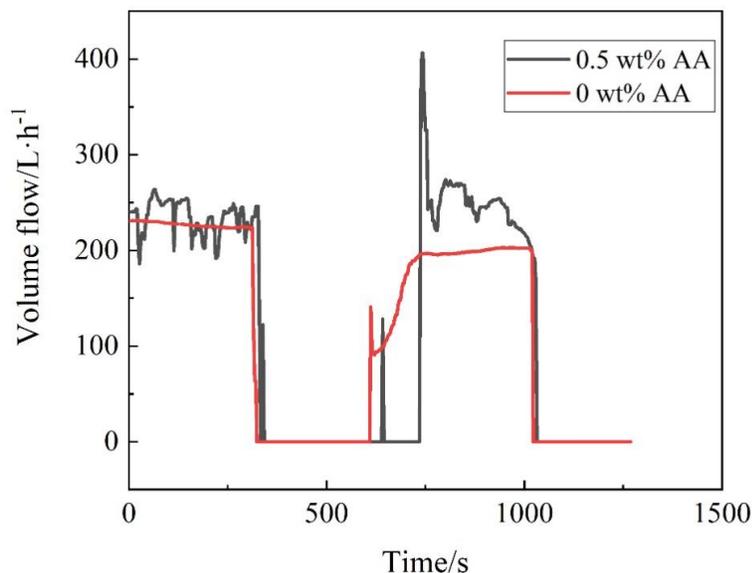
In order to further explore the anti-agglomeration performance of the new Anti-agglomerants under the condition of inclined pipe, the plugging time of the system with or without Anti-agglomerants under the conditions of flow rate of 230 L / h, water content of 100 % and pipe inclination of 10° relative to the horizontal plane was experimentally explored. **Fig. 7** shows the flow curve of the system under the pure water condition of inclined pipe. The plugging time of hydrate slurry without AA and with 0.5 wt % AA

was 18 min and 33 min, respectively. Obviously, under the condition of inclined tube, the polymer inhibitor still has excellent anti-coagulation effect. In addition, compared with Fig. 4, it can be seen that the plugging time of hydrate in inclined pipe system is shorter than that in horizontal pipe system. This may be due to the small flow at the dead angle of the inclined pipe, which is prone to hydrate accumulation, resulting in flow blockage and pressure drop increase. The exfoliated hydrate deposits are also easy to accumulate and deposit at the dead angle, so the blockage risk of inclined pipelines is generally higher than that of straight pipelines.



**Fig. 7-Flow curve of system under inclined tube condition**

**3.4 Flow characteristics of hydrate slurry under shutdown and restart conditions.** In order to simulate the working condition of shutdown and restart in the actual pipeline, the phenomenon is simulated by shutdown and restarting the pump during the experiment. In addition, the influence of polymer inhibitor on the flow characteristics of pipeline shutdown and restart was also explored. The **Fig.8** shows the slurry flow curve in the loop shutdown restart system with and without Anti-agglomerants agent. The two systems shut down the pump at 5min after cooling, and start the pump again at 5min. In the system without Anti-agglomerants agent, the flow rate of hydrate slurry drops to 0 automatically after 7 minutes of operation. In the system with 0.5 wt % Anti-agglomerants agent, the hydrate slurry can still flow smoothly after 7 minutes of restart, and the flow rate is reduced to 0 by manually shutting down the pump. Although the flow rate can not return to normal after the second shutdown, the new Anti-agglomerants agent can ensure that the flow time of hydrate slurry is longer than that of pure water system after the first shutdown and restart. The flow rate of the system with Anti-agglomerants agent fluctuates greatly, and the flow rate is 0 after the initial restart. The reason has been mentioned in the above.



**Fig. 8-Flow curves in the system with and without Anti-agglomerants agent under shutdown and restart conditions**

First, CO<sub>2</sub> hydrates need induction time before random crystallization and nucleation. After the induction period, CO<sub>2</sub> hydrate began to form and grow rapidly on the wall. Since the temperature at the pipe wall is lower than that at the flow center, only a small amount of hydrate is formed in the liquid body. Due to the hydrophilic surface of hydrate particles, CO<sub>2</sub> hydrates continue to form, aggregate and adhere to the formed thin hydrate layer. The viscous and moist surfaces of the two CO<sub>2</sub> hydrate layers become thicker and thicker, and the flow area decreases. Then, the system was shut down and restarted. Due to the sudden increase of pump frequency, the increase of flow promoted and destroyed some of the non-compact deposits. Secondly, as the liquid phase begins to flow again, it provides better mass and heat transfer conditions for hydrate formation, thus promoting the formation, growth and adhesion of a large number of hydrates to the wall and the previously formed hydrate layer. This leads to a decrease in the flow cross section at the location of the previously formed hydrate layer. The new hydrate layer will also adhere and deposit on the wall. Finally, for the blockage after pump shutdown, even if the pump frequency is restored to the initial value, the driving force of the flow will decrease. With the continuous formation of a large number of CO<sub>2</sub> hydrates, secondary deposition occurs at the position of the first hydrate layer. Due to the compaction of accumulated CO<sub>2</sub> hydrates, the plugging cannot be irreversible by adjusting the pump frequency to the flow rate of the original system. At the same time, other new hydrate layers and plugging points are formed in the flow circuit, which also aggravate the risk of hydrate plugging. **Fig. 9** shows the schematic diagram of hydrate blockage process under shutdown and restart conditions.

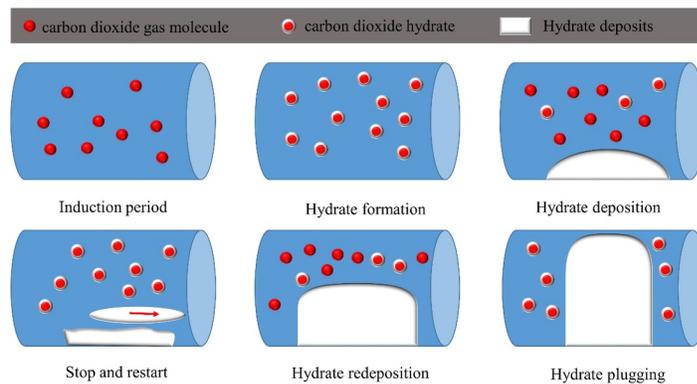


Fig. 9-The schematic diagram of hydrate blockage process under shutdown and restart conditions

### Conclusion

In this work, the effect of new anti-agglomeration agent ( coconut oil amide propyl betaine ) on the flow stability of oil-water emulsion system under different water contents and flow rates was explored, and it was confirmed that the new anti-agglomeration agent under high water content or even pure water conditions can still play an anti-agglomeration role, so that hydrates can form stable and mobile mud. In addition, in order to explore the parameter changes in the system caused by the transient changes ( shutdown and start ) in the flow system and the flow characteristics of hydrate in the non-flat pipeline, the flow characteristics of hydrate slurry with inclined pipe section are explored, and the changes in the flow characteristics of hydrate with shutdown and restart in the actual production process are explored by stopping and restarting the equipment. The specific research results are as follows :

Coconut oil amide propyl betaine can be used as an excellent anticoagulant to prolong the plugging time of hydrate under pure water conditions. However, when it plays a role, it will generally make the flow in the system fluctuate significantly and irregularly. This may be caused by the change of hydrate aggregation state by the inhibitor. The specific mechanism still needs further study to supplement the insufficient understanding of the anti-aggregation process mechanism of the inhibitor. The water content can affect the liquid bearing capacity and the unit solubility of the hydrate formation region. The initial flow rate will change the gas-water mass transfer efficiency during hydrate formation and the shear force on the hydrate layer on the wall. The increase of water content and initial flow rate will prolong the plugging time of hydrate. The conclusion can be used as a theoretical support for mobility support technology. The plugging time of inclined pipe is usually shorter than that of the straight pipe with the same inclination condition, which may be due to the existence of dead angle in inclined pipe and the accumulation of exfoliated hydrate sediments, leading to a sharp increase in pressure drop. It is necessary to further develop the flow support technology for inclined pipes to ensure the stable operation of energy transmission in unconventional pipe sections. Adding polymer inhibitor can prolong the plugging time after shutdown and restart, and the plugging mechanism of hydrate from formation to plugging in the system of shutdown and restart is drawn.

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## References

- Baek, S., Ahn, Y. H., Zhang, J., Min, J., Lee, H., & Lee, J. W. (2017). Enhanced methane hydrate formation with cyclopentane hydrate seeds. *Applied Energy*, 202, 32-41.
- Dong, S., Liu, C., Han, W., Li, M., Zhang, J., & Chen, G. (2020). The effect of the hydrate antiagglomerant on hydrate crystallization at the oil–water interface. *ACS omega*, 5(7), 3315-3321.
- Wu, Y., Shang, L., Pan, Z., Xuan, Y., Baena-Moreno, F. M., & Zhang, Z. (2021). Gas hydrate formation in the presence of mixed surfactants and alumina nanoparticles. *Journal of Natural Gas Science and Engineering*, 94, 104049.
- Sun, M., & Firoozabadi, A. (2013). New surfactant for hydrate anti-agglomeration in hydrocarbon flowlines and seabed oil capture. *Journal of colloid and interface science*, 402, 312-319.
- Phan, A., Stamatakis, M., Koh, C. A., & Striolo, A. (2021). Correlating Antiagglomerant Performance with Gas Hydrate Cohesion. *ACS Applied Materials & Interfaces*, 13(33), 40002-40012.
- Gao, S. (2009). Hydrate risk management at high watercuts with anti-agglomerant hydrate inhibitors. *Energy & Fuels*, 23(4), 2118-2121.
- Sun, M., & Firoozabadi, A. (2014). Natural gas hydrate particles in oil-free systems with kinetic inhibition and slurry viscosity reduction. *Energy & fuels*, 28(3), 1890-1895.
- Zhao, H., Sun, M., & Firoozabadi, A. (2016). Anti-agglomeration of natural gas hydrates in liquid condensate and crude oil at constant pressure conditions. *Fuel*, 180, 187-193.
- Li, M., Dong, S., Li, B., & Liu, C. (2018). Effects of a naturally derived surfactant on hydrate anti-agglomeration using micromechanical force measurement. *Journal of Industrial and Engineering Chemistry*, 67, 140-147.
- Dong, S., & Firoozabadi, A. (2018). Hydrate anti-agglomeration and synergy effect in normal octane at varying water cuts and salt concentrations. *The Journal of Chemical Thermodynamics*, 117, 214-222.
- Zhang, W., Jin, H., Du, Q., Xie, K., Zhang, B., Zhang, X., & Li, H. (2021). Assessment of hydrate flow obstacles during the initial restarting period of deep-water gas wells. *Heat and Mass Transfer*, 57(11), 1737-1751.
- Kakitani, C., Marques, D. C., Marcelino Neto, M. A., Teixeira, A., Valim, L. S., Morales, R. E., & Sum, A. K. (2019). Measurements of hydrate formation behavior in shut-in and restart conditions. *Energy & Fuels*, 33(10), 9457-9465.
- Kakitani, C., Marques, D. C., Teixeira, A., Valim, L., Neto, M. A. M., Sum, A. K., & Morales, R. E. (2022). Experimental characterization of hydrate formation in non-emulsifying systems upon shut-in and restart conditions. *Fuel*, 307, 121690.
- Shuard, A. M., Mahmud, H. B., & King, A. J. (2017). An optimization approach to reduce the risk of hydrate plugging during gas-dominated restart operations. *Journal of Petroleum Science and Engineering*, 156, 220-234.
- Sohn, Y. H., & Seo, Y. (2017). Effect of monoethylene glycol and kinetic hydrate inhibitor on hydrate blockage formation during cold restart operation. *Chemical Engineering Science*, 168, 444-455.
- Shi, B. H., Ding, L., Li, W. Q., Lv, X. F., Liu, Y., Song, S. F., & Gong, J. (2018). Investigation on hydrates blockage and restart process mechanisms of CO<sub>2</sub> hydrate slurry flow. *Asia-Pacific Journal of Chemical Engineering*, 13(3), e2193.
- Liu, Z., Liu, Z., Wang, J., Yang, M., Zhao, J., & Song, Y. (2021). Hydrate blockage observation and removal using depressurization in a fully visual flow loop. *Fuel*, 294, 120588.

Yan, K. L., Sun, C. Y., Chen, J., Chen, L. T., Shen, D. J., Liu, B., & Chen, G. J. (2014). Flow characteristics and rheological properties of natural gas hydrate slurry in the presence of anti-agglomerant in a flow loop apparatus. *Chemical Engineering Science*, 106, 99-108.

Liu, Z., Liu, Z., Wang, J., Yang, M., Zhao, J., & Song, Y. (2021). Hydrate blockage observation and removal using depressurization in a fully visual flow loop. *Fuel*, 294, 120588.

Zhang, S. W., Pan, Z., Shang, L. Y., & Zhou, L. (2021). Analysis of Influencing Factors on the Kinetics Characteristics of Carbon Dioxide Hydrates in High Pressure Flow Systems. *Energy & Fuels*, 35(19), 16241-16257.

Shi, B., Ding, L., Liu, Y., Yang, J., Song, S., Wu, H., & Gong, J. (2018). Hydrate slurry flow property in W/O emulsion systems. *RSC advances*, 8(21), 11436-11445.

Zhang, S. W., Shang, L. Y., Zhou, L., & Lv, Z. B. (2022). Hydrate Deposition Model and Flow Assurance Technology in Gas-Dominant Pipeline Transportation Systems: A Review. *Energy & Fuels*. 36,(4), 1747-1775.