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ARTICLE

Investigation of the performance of low-dosage hydrate inhibitors combined with wax inhibitors for a mixed CH_4-CO_2 gas hydrate formation

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Within the oil and gas industry, low-dosage hydrate inhibitors (LDHIs) are a proven technology to control hydrates. Besides hydrate inhibitors, wax inhibitors (WIs) are frequently injected to prevent wax buildup in the crude oil pipeline. However, little attention has been focused on the effect of wax inhibitors on the performance of LDHIs. In this study, performance tests of 3 LDHIs in the presence of wax inhibitors were carried out for a 67% CH_4/33% CO_2 gas hydrate formation. Using the isothermal cooling method at pressures of 9 MPa and temperatures of 4 °C (subcooling is 9 °C), the results showed that the induction time of CH_4-CO_2 gas hydrate formation with LDHI/WI was shorter than the system with only LDHI. During the growth period, when the concentration of the WIs was 1 mass%, the growth time of the system with LDHI/WI was prolonged. Taking the induction time and the growth time into consideration, it was found that WIs had a more negative impact on the kinetic hydrate inhibitor performance at low dosage. The effect of WIs at high concentration could be negligible.

Key words: gas hydrate, low-dosage hydrate inhibitor, wax inhibitor, CO_2-rich gas, induction time.

Au sein de l'industrie pétrolière, l'utilisation d'inhibiteurs d'hydrates à faible dose est un moyen reconnu pour maîtriser la formation d'hydrates. Outre les inhibiteurs d'hydrates, des inhibiteurs de cire sont couramment injectés pour prévenir la formation de cire durant le transport du pétrole brut dans les pipelines. Toutefois, les effets des inhibiteurs de cire sur le rendement des inhibiteurs d'hydrates à faible dose ont peu été étudiés. Dans la présente étude, à l'aide d'une méthode de refroidissement isotherme, à une pression de 9 MPa et une température de 4 °C (température de sous-refroidissement de 9 °C), nous avons évalué le rendement de trois inhibiteurs d'hydrates à faible dose en présence d'inhibiteurs de cire dans des essais portant sur la formation d'hydrates de gaz composés à 67 % de méthane (CH_4) et 33 % de dioxyde de carbone (CO_2). Les résultats ont révélé que la période d'induction de la formation des hydrates de CH_4 et CO_2 en présence des deux types d'inhibiteurs était plus courte que dans le système comportant seulement un inhibiteur d'hydrates à faible dose. Au cours de la période de croissance, lorsque la concentration de l'inhibiteur de cire représentait 1 % p/p, la période de croissance dans le système en présence des deux types d'inhibiteurs était prolongée. En prenant en compte les périodes d'induction et de croissance, nous avons constaté que les inhibiteurs de cire avaient des effets plus délétères sur le rendement des inhibiteurs cinétiques lorsque ceux-ci étaient utilisés à faible dose, alors qu'à concentration élevée, l'effet des inhibiteurs de cire pourrait être négligeable. [Traduit par la Rédaction]

Mots-clés : hydrate de gaz, inhibiteur d'hydrates à faible dose, inhibiteur de cire, gaz enrichi en CO_2, période d'induction.

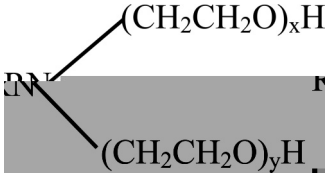
Introduction

The crystalline structures of gas hydrates composed of small gas

are different mechanisms of wax prevention by paraffin inhibitors. Possible ways of preventing deposition of paraffin are: increasing the wettability of the surface on which the wax are deposited and creating conditions unfavorable to deposition of wax on the pipe walls; prevention of growth of wax crystals by modifying their structure.[19,20] Perhaps the most effective way of dealing with the problem of wax deposition in pipelines is to prevent it from occurring in the first place.

To solve the hydrate and wax problem simultaneously, both LDHIs and wax inhibitors are needed, which could possibly lead to incompatibilities. There have been a few studies on the interaction of these two kinds of inhibitors. Swanson et al. reported the successful use of both KHIs and WIs.[21] However, a problem exists because incompatibilities can emerge with different wax inhibitor and LDHI combinations. Thus, our work studies the effect of wax inhibitors on the performance of selected LDHIs (KHIs or AAs).

In this study, we used commercial inhibitor Inhibex501 (ISP), synthesized inhibitor HY-1,[22] and anti-agglomerant KL-1and two WIs, WJH-01 and BHFL-02, synthesized by CNOOC Energy Technology & Services, Oilfield Technology Services. The chemical structures of Inhibex501 and HY-1 are given in Figs. 1 and 2, respectively. The major component of KL-1 is a surfactant. WJH-01 mainly contains poly ether carboxylate ($RO(CH_2CH_2O)nCH_2COONa$) and poly ether carboxylic acid esters ($RCOO(CH_2CH_2O)nCH_2CH_3$). BHFL-02 mainly contains alkyl poly ether carboxylate ($RO(CH_2CH_2O)nCH_2COONa$) and poly ether alkyl amine. The molecular formula of poly ether alkyl amine is:



The testing gas was CH_4-CO_2 (33%) mixture gas, which simulates the DongFang field gas in the South China Sea.

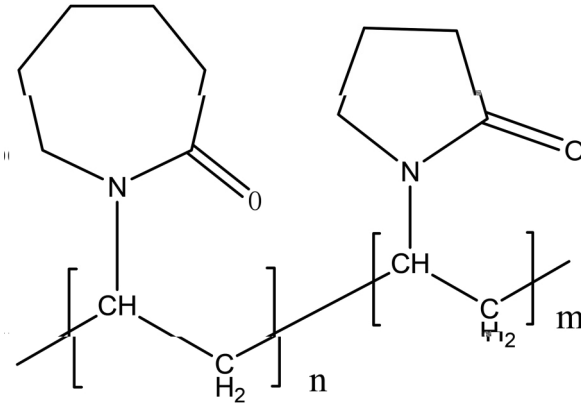
Experimental

The materials used in the experiments are shown in Table 1. The concentration of the mixture gas was analyzed by Gas Chromatography (GC). HY-1 was synthesized by free-radical polymerization of *N*-vinyl–2-pyrrolidone in diethylene glycol monobutyl ether.[22] Inhibex501 (vinyl caprolactam/vinylpyrrolidone copolymer in butoxyethanol solution ($w = 0.5$) is a commercial KHI. KL-1 is a type of AA supplied by China University of Petroleum. WJH-01 and BHFL-02 are common wax inhibitors. Distilled water used in this study was weighed on an electronic balance with an accuracy of ±0.1 mg and measuring range is 0–220 g.

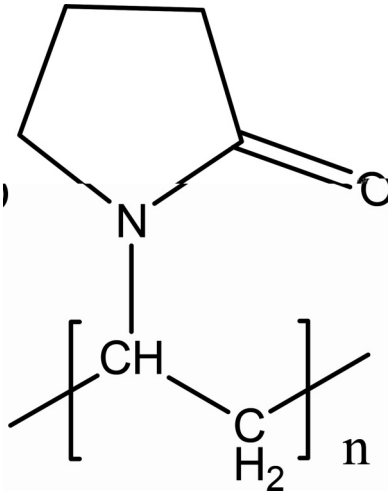
The schematic diagram of the experimental apparatus[23] is shown in Fig. 3. We used it to evaluate the performance of LDHIs on the CO_2-rich gas. The apparatus contains 6 identical magnetic-stirred steel cells, and the volume of each is 100 mL. The refrigeration chamber (Xutemp Temptech Co., Ltd. Hangzhou, China) provides a cold air bath, and the temperature is less than 0.5 °C. Thermocouples (type J) with an accuracy of ±0.1 °C were placed to measure the temperature. The pressure was measured by the transducer (Senex DG-1300) with an accuracy of ±0.01 MPa. All experimental data were recorded by a data logger (Agilent 34970A).

The induction time and growth time of gas hydrate with different LDHIs were tested using the isothermal cooling method.[24] The deionized water with additives was prepared first. Then 40 g solutions were put in the pressure cells. The temperature of the chamber was raised to 30 °C and kept for 30 min. Then the CH_4-CO_2 gas was pumped into the cells to 9 MPa (phase equilibrium point of the mixture gas is 13 °C). Finally, the chamber was cooled continuously to around 4 °C (subcooling temperature is about 9 °C), which simulates the subsea temperature. Stirring was then started at 550 rpm.

. . . Chemical structure of Inhibex501 (major component).



. . . Chemical structure of HY-1 (major component PVP).



Results and discussion

Induction time is the most critical parameter to rank the performance of LDHIs. At least two parallel experiments were carried out to reduce deviation of results. The pressure and temperature data of the mixture gas + water versus time using the isothermal cooling method in an experiment are shown in Fig. 4.

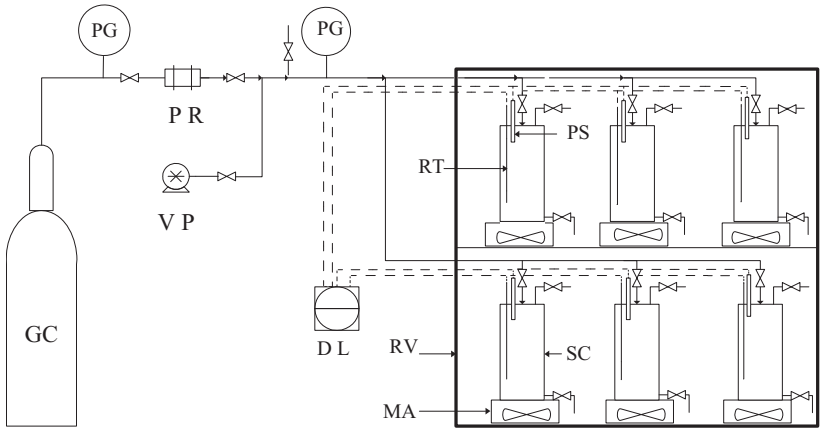
In Fig. 4, we can see that the temperature drops at a constant rate until the expected 4 °C. During the cooling period, the pressure also drops at a constant rate. As the figure shows, we defined the start time of experiment as time zero, and t_b is the start time of cooling; t_c is the time that nucleation starts, in which there is a sudden increase in temperature and a significant drop of pressure; t_d is the time when the catastrophic hydrate formation is finished. The induction time t_0 is defined as the difference between t_c and t_b, $t_0 = t_c - t_b$. The growth time t_a is defined as the difference between t_d and t_c, $t_a = t_d - t_c$.

The effect of wax inhibitors on the blank (without hydrate or wax inhibitors) system was summarized in Fig. 5. As Fig. 5 shows, the average induction time shows almost no difference between the system with 1% WJH-01 (3.95 h) and with deionized water

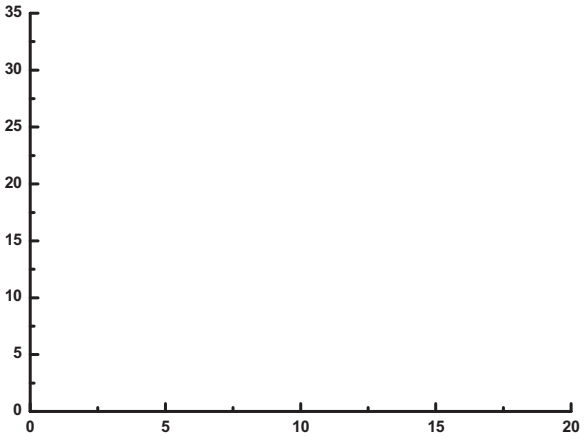
. Experiment materials used in this work.

Component	Purity	Supplier
CH_4-CO_2 gas	0.67 and 0.33(mole fraction)	Guangzhou Zhuozheng Gas Industry Co., Ltd.
HY1	W≧0.99	South China University of Technology
Inhibex501	w≧0.999	ISP International Specialty Products Inc, USA
KL-1	w≧0.99	China University of Petroleum
WJH-01	w≧0.99	CNOOC Energy Technology & Services-Oilfield Technology Services Co.
BHFL-02	w≧0.99	CNOOC Energy Technology & Services-Oilfield Technology Services Co.
Deionized water	—	

. . Low-dosage hydrate inhibitor performance evaluation apparatus. GC-gas cylinder; VP-vacuum pump; PG -pressure gauge; PRpressure regulator; PS-pressure sensor; RT-resistance thermometer; DL-data logger RV-refrigeration vessel; SC-Steel cell; MA-magnetic agitator.



. . Temperature and pressure evolution of CH_4-CO_2 gas with distilled water during the isothermal cooling test.

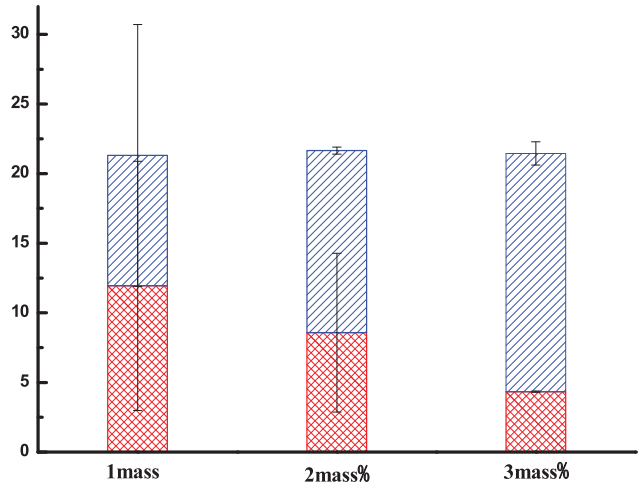


(3.7 h), while the induction time of the system with 1% BHFL-02 (5.21 h) is a little longer, which means there is a weak influence on the CH_4-CO_2 gas hydrate formation. Additionally, both wax inhibitors can prolong the gas hydrate growth time. The 1% WJH-01 can prolong the growth time (5.89 h) longer than 1% BHFL-02 (3.94 h).

Using the isothermal cooling method and the same experimental condition, the induction and growth time of HY-1, Inhibex501, and AA at different concentrations (1 mass%, 2 mass%, and 3 mass%) were tested and results are displayed in Fig. 6, Fig. 7 and Fig. 8, respectively. In Fig. 6, the average induction time t_0 of 1 mass%, 2 mass%, and 3 mass% HY-1 were 11.94, 8.58, and 4.34 h, respectively, and the average growth times were 9.37, 13.085, and 17.12 h, respectively. When the concentration of HY-1 increased, the induction time decreased, and the growth time was prolonged. In the case of KL-1, there is a clear statistical trend to shorten induction time when the concentration of KL-1 increases. It is noteworthy that the gas hydrate with KL-1 was growing all the time till the end of the experiment. Because KL-1 is a surfactant, it allows hydrates to form but prevents the hydrate crystals from agglomerating and subsequently accumulating into large masses. For the ISP-501 system, when the concentration of ISP-501 is 3 mass%, the average induction time is the longest, 7.32 h (Fig. 7). It is worth mentioning that ISP-501 can delay hydrate formation, but after the start of the formation, it will accelerate the dosage of the hydrate.

Figures 9, 10, and 11 show the effect of wax inhibitors (WJH-01 and BHFL-02) in different concentrations on the induction and

. . Induction and growth time at varying concentrations of HY-1.



growth time of gas hydrate formation with HY-1, ISP-501, and KL-1, respectively.

To evaluate the effect of WI on LDHI performance, a "% Performance" scale of the LDHI was developed.[25] In our work, "% Performance" was determined by induction time and growth time. We defined performance on the induction time as "PI", "% Performance" determined by the induction time as "%PI", performance on the growth time as "PG", "% Performance" determined by the growth time as "%PG". Then the "% Performance" is the mean value of %PI and %PG.

The concentrations of HY-1, ISP-501, and KL-1 in this study were 1 mass%, 3 mass%, and 1 mass%, which produce the longest average induction times of 11.94, 8.27, and 7.32 h, respectively. The %PI of HY-1, ISP-501, and KL-1 at that induction time was designated as 100%. In the same way, the percent performance without LDHI was designated as 0%. Using eq. 1, %PIof any WI + LDHI combination can be calculated by the induction time of the system with WI and LDHI.

$$\%PI = \frac{\text{Induction time of the system with WI + LDHI}}{\text{Induction time of the system with LDHI}} \times 100 \quad (1)$$

Using this equation, the impact of each WI on the LDHI performance determined by the induction time (PI) can be calculated. For example, the induction time of the system with 1mass% HY-1 was 11.94 h, with 0.1 mass% WJH-01 + 1 mass% HY-1 was 4.185 h. Applying eq. (1), the %PI of HY-1 in the presence of 0.1 mass% WJH-01 was 35%. Namely, adding 0.1 mass% WJH-01 to the 1 mass% HY-1 reduced the PI of HY-1 by 65%. This means that the lower the %PI of HY-1 in the presence of WI, the greater effect on HY-1.

The %PI of three LDHIs (HY-1, ISP-501, and KL-1) combined with two WIs (WJH-01 and BHFL-02) at 0.1 mass% and 1 mass% are summarized in Table 2. The effect of all WIs on the PI of the LDHIs is clearly negative. The results were not so consistent with Swanson et al.[21] Overall, WI additives disadvantaged delay nucleation with KHIs (HY-1 and ISP-501) at 0.1 mass% than at 1 mass%, as shown in Table 2. Furthermore, increasing the concentration of WJH-01 decreased the PI of the AA (KL-1) to a greater degree. It is worth noting that when the concentration was 0.1 mass%, WJH-01 had almost no effect. BHFL-02 at a dosage of 0.1 mass% and 1 mass% had a same influence on the PI of KL-1, while the concentration of WI did not have a regular impact on PI. For instance, WJH-01 and BHFL-02 had very different influences on the performance of the KL-1 at 0.1 mass% concentration. BHFL-02 had a significant effect on the PI of KL-1, bringing the %PI down to 40%, while WJH-01 had no impact. In general, WJH-01 had a more negative impact on the

combination with WIs. The results showed that when the concentration of HY-1, ISP-501, and KL-1 was 1 mass%, 3 mass%, and 1 mass%, the average induction time of the gas system was the longest, at 11.94, 7.32, and 8.27 h, respectively. The performance of LDHIs was significantly reduced in the presence of WIs at low concentration. The effect of WIs at high concentration can be negligible. This may be related to the adsorption of WIs on the polymer. When the concentration is high, the surfactants will play a role, which will affect the growth process. However, further tests are required to verify the experiment mechanism.

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