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Kinetic hydrate inhibitor leads to a reduction of 80% in MEG usage and 40% in MEG flowrate

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Abstract
Multiple experimental testing and modeling studies have been performed to successfully demonstrate that the addition of Kinetic Hydrate Inhibitors (KHIs) can significantly reduce the overall usage of Monothylene Glycol (MEG) and the size of the MEG reclamation unit thereby effectively reducing CAPEX and OPEX. MEG is a thermodynamic hydrate inhibitor but has a required dose rate of as high as 60 wt.% based on the overall water, which leads to large pipeline and reclamation units. A series of performance tests were undertaken in a high-pressure rocking cell to evaluate the effect of the combination of KHI and MEG in hydrate induction times. Positive results revealed that the MEG dose rate may be reduced by up to 80% with less than 2 vol.% KHI added into the system. This reduction in the required MEG dose rate leads to a 40% reduction in the flow rate of rich MEG to the MEG recovery unit. Furthermore, in the evaluation process, it was established that the activity of the KHI after severe heating at 160°C was maintained and that the KHI might be reused to further reduce the total chemical cost for the flowline.

Keywords
Hydrates; Kinetic Hydrate Inhibitor; Reclamation

Introduction
Gas hydrates are crystalline solid compounds consisting of a three-dimensional lattice of hydrogen-bonded water and gas molecules (e.g., methane, carbon dioxide, hydrogen, etc.) formed at high-pressure and low-temperature conditions. Typical gas hydrates are classified into three crystal structures: cubic structure I (sI), cubic structure II (sII), and hexagonal structure (sH).[1]
Gas hydrates provide the possibility of carbon dioxide (CO_2) transportation and storage, due to a high storage density of approximately 175 volumes of CO_2 per volume of hydrate.[2] However, gas hydrates can be formed in subsea oil and gas wells and flowlines because the operating conditions include high pressure and low temperature at which gas hydrates are thermodynamically stable. The deposition and agglomeration of gas hydrates can subsequently plug the flowlines, resulting in disruption to production, economic losses, and adverse environmental impacts. Hydrate inhibitors were developed to provide prevention and mitigation strategies for the potential hydrate issues. Thermodynamic hydrate inhibitors (THIs) are the most commonly used hydrate inhibitors to prevent hydrate formation.[1,3] THIs can prevent hydrate formation by shifting the operating conditions outside of the hydrate stability zone. Common THIs are methanol and monoethylene glycol (MEG). However, the required dose rate of MEG can be as high as 60 wt.% based on the overall amount of water, which leads to a large pipeline and reclamation unit.[2,4] MEG reclamation units are usually utilized to purify the rich MEG which contains salts and water in the stream; then regenerate the rich MEG into a lean, high purity and salt-free MEG for recirculation to the flowline to prevent hydrate formation. MEG reclamation unit design is dependent on the hourly MEG injection rate. A high MEG injection rate leads to a larger unit footprint, ultimately increasing the cost and schedule to build units. In most cases, the reclamation units need to be designed and sized for a small operating window in the life of the asset, meaning that the unit is oversized for the majority of its operational lifetime. Therefore, to reduce the usage of MEG thereby minimizing the size of the MEG reclamation units, kinetic hydrate inhibitors (KHIs) are introduced into the system. KHI, classified as a low dosage hydrate inhibitor (LDHI), can be effective at 1-2 vol.% of water. The system can be protected kinetically by increasing the hydrate induction and growth times.[5]
A series of performance tests were undertaken in a high-pressure rocking cell to evaluate the effect of the combination of KHI and MEG in hydrate

induction times. Compared to the information from the field, which currently injects over 50 vol.% MEG for hydrate treatment results revealed that the MEG dose rate could be reduced by up to 80% with less than 2 vol.% KHI added into the system. This reduction in the required MEG dose rate leads to a 40% reduction in the flowrate of rich MEG (including MEG, water, dissolved salts and KHI) to the MEG recovery unit where the water and salt present in the flowline MEG are removed to yield a lean MEG product suitable for re-injection. Based on a production estimation of 4,000 BPD water, the weight of the top-side equipment is estimated to be reduced by 15%.

Furthermore, experiments were also conducted to evaluate KHI performance after severe heating at 160°C to evaluate the potential for the KHI to be recirculated and reinjected. The temperature was selected to simulate the condition inside the MEG recovery unit. From the initial testing, it was found that the activity of the KHI after heat treatment was substantially maintained and that the KHI might therefore be reused to further reduce the total chemical cost for the flowline.

Methodology

This section illustrates the detailed experimental procedures of the rocking cell testing and the high-temperature stability testing of the KHIs.

Experimental Procedure

Rocking Cell

The rocking cell apparatus used in this study tests the performance of KHI in the presence of MEG. The system allows the mixing of oil, water, gas and hydrate inhibitors (and/or other production chemicals) at the desired pressure and temperature where hydrates are formed. By tilting, an inserted ball moves through the entire length of the testing cell and improves the mixing of all components. The ball movement introduces shear forces and turbulence inside the test cell, which aims to mimic the conditions inside a flowline.

The cells are mounted on a movable axle, inside a bath of cooling liquid. For a test, the cells are filled with sample fluid (e.g. oil/condensate, gas, brine) and the desired dose rates of inhibitor; subsequently, they are cooled to the target temperature. Each cell can be subsequently individually pressurized up to 2900 psi. All test parameters such as cooling rate, rocking angle, rocking rate and test length can be scheduled via software. A camera can record pictures and videos at any time during the experiment.

In this study, a pressure of 1350 psi and a temperature of 5°C were used as the final condition for hydrate testing, which reflects a subcooling (the temperature difference between the operating and hydrate equilibrium temperatures at fixed pressure) of 8°C. The brine consisted of 1 wt.% NaCl and 0.5 wt.% $CaCl_2$. The gas composition, which results in sI hydrates formation, is shown in Table 1. A minimum protection time of 72 hr was required for any candidate KHI to pass the test.

Table 1. Gas composition that forms sI hydrate

Component	Concentration (mol.%)
Methane	97
Ethane	1
Carbon Dioxide	1
Nitrogen	1

High-Temperature Stability Testing

As most KHIs contain active materials that are polymeric, they can precipitate out when the temperature increases, which leads to a reduction in performance. Hence, the high-temperature stability testing aimed to determine if a KHI can maintain optimal performance in delaying hydrate formation onset after severe heating.

Firstly, the final formulated products were placed in a sealed aging cell at a temperature of 140°C for 3 days. Then the samples were injected into rocking for re-testing at the desired conditions.

To test the products under even more severe conditions, the raw KHI active alone was placed on a hot plate at 160°C to remove the solvent that was present in the neat product. This step leads to dry solids inside the container. The solids were then re-dissolved with proper solvents. This re-dissolved material subsequently had the same activity compared to the initially formulated product that was tested.

Results and Discussion

Baseline Testing

A series of baseline testing was performed without the addition of KHI to evaluate the required MEG dose rate at the desired pressure and temperature conditions. The MEG dose rate was increased from 0 vol.% to 100 vol.% by volume of water. It was found that at least 33 vol.% MEG was needed to treat the system without any support from the KHI. This result was used in the following sections when determining how much MEG can be reduced with the addition of KHI.

Product selection

As the performance of any KHI is influenced by many parameters such as gas composition, salinity, etc., multiple testing was conducted to screen for the optimal product for this particular scenario. A total of 4 products were selected as candidates for rocking cell testing. To ensure a direct comparison, the concentration of the active components in each product remained constant. For comprehensive screening, different combinations of KHI and MEG were tested. From the initial screening and repeat tests, 2 candidates, Chemical 1 and Chemical 2, were selected for the next step due to the long induction time.

Final candidate results

Testing was conducted and duplicated to ensure the performance of the two selected candidates, Chemical 1 and Chemical 2. As shown in Table 2, several combinations of the KHI and MEG concentrations were tested. Both products were able to protect the system from hydrate formation for at least 72 hr. Clearly, with the help of a small dosage of KHI, the total required MEG can be reduced from 50 vol.% (currently injected) to 10 vol.%, leading to an 80% saving on MEG usage.

Product	KHI (vol.%)	MEG (vol.%)	Testing results
Chemical 1	3	5	Fail
	2.5	10	Pass
	2	10	Pass
	1.5	15	Pass
	1.25	15	Pass
Chemcial 2	3	5	Pass
	2.5	10	Pass
	2	10	Pass
	1.5	15	Pass
	1.25	15	Pass

High-temperature stability results

The results of the high-temperature stability testing are shown in Table 3. Initially, the final formulated products were sealed in a stainless-steel aging cell for 3 days. The samples were subsequently injected into the rocking cell at the same dose rates shown in Table 2. It was found the performance of the products did not reduce due to thermal aging under the conditions used. From this testing, Chemical 2 was selected to proceed due to the slightly superior performance compared with Chemical 1.

As discussed in the previous section, Chemical 2 was dried at 160°C. The solid material generated was re-dissolved with solvents and injected into the rocking cell. As shown in Table 3, no reduction in performance was observed with the addition of the dried and re-dissolved Chemical 2. This method was used to mimic the processes inside the rich MEG reclamation unit. It can also be used to test the reusability of the candidate after severe heating. The results of the testing reveal that the product may be reused after being heating and filtered in the MEG reclamation system.

Table 3. High-temperature stability results

Product	Temp. (°C)	Duration (hr)	Performance reduction?
Chemical 1	140	72	No
Chemical 2	140	72	No
Chemical 2	160	1	No

Conclusions

Multiple experimental testing and modeling studies have been performed to successfully demonstrate that the addition of KHIs can significantly reduce the overall usage of MEG and the size of the MEG reclamation unit thereby effectively reducing CAPEX and OPEX. It was found the addition of 1.5 vol.% KHI Chemical 2 can effectively reduce the MEG usage by 80% and also present a long induction time. High-temperature testing was also conducted to test the reusability of the KHI. Results indicated that the products may be able to be recirculated and reused after being heated in the MEG reclamation system.

These results will be applied by the Engineering Team to evaluate the cost and schedule reduction impact due to the size reduction of the pipeline and the topside MEG recovery facilities. Further work is being carried out to mimic the KHI in the MEG recovery unit’s flash vessel and distillation tower. These tests will allow the Engineering and Production Chemistry teams to evaluate the feasibility of (1) recycling unrecovered KHI back to the flowline along with Lean MEG and (2) recovering the KHI active components from the process, re-formulating the KHI and then injecting the recovered KHI to the flowlines with the Lean MEG product from the MEG Recovery Package.

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