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Preventing gas hydrate plugging in deepwater wells

Low-dosage hydrate inhibitors are an alternative technology to thermodynamic inhibitors for preventing gas hydrates from restricting production from deepwater wells. Injecting the correct amount of a high-performance chemical has proven effective at mitigating unplanned shut-ins and the resulting loss of production revenue.

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Gas hydrate plugging is a major concern for offshore oil and gas production, especially in deepwater operations. Gas hydrate plugging negatively impacts production and causes significant safety risks during remediation. Gas hydrates are an ice-like solid structure, consisting of water enclathrating low-molecular-weight natural gases. Gas hydrates are typically stable at conditions of high pressure and low temperature.

Of the options that exist to deal with gas hydrate risk, only a limited sub-set of technology is applicable for subsea deployment, due to the extreme conditions or cost (capital and operational).

Chemical treatment is frequently applied for the control of hydrate risk in the form of hydrate inhibitors. Two inhibitor types are to be distinguished: Thermodynamic hydrate inhibitors (THIs) and low-dose hydrate inhibitors (LDHIs), which are further divided into kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs). Field application of AA technology is discussed further in this article.

Hydrates that form after an AA treatment will be transportable as a slurry of hydrate particles dispersed in the hydrocarbon phase. The viscosity of the hydrate slurry needs to be kept at a level that still allows for easy flow. Water cuts approaching approximately 60% become challenging, but they can still be effectively treated, and examples of successful treatments in fields with water cuts of 85% to 90% exist, e.g. in the Gulf of Mexico (Kelland 2006; Miller 2016).

Key parameters have been identified and understood to allow the development of accurate and robust testing protocol, such as water cut, salinity, gas composition, degree of subcooling (defined as the temperature difference between operational temperature and the hydrate equilibrium temperature at a specific operational pressure) and gas-to-oil ratio (GOR). These parameters are taken into consideration when defining the testing protocol to verify the efficiency of the chemical at critical conditions.

Testing methodologies. There are several industry-accepted test equipment items and methods to determine the efficacy and minimum effective dose (MED) of AAs. Each must be chosen appropriately, depending on the specific field conditions in consideration. Equipment commonly used when conducting AA evaluation is the high-pressure rocking cell. This equipment typically contains steel or sapphire cells that vary in volume from approximately 10 mL to 50 mL. The cell commonly contains a steel ball and is rocked back and forth to create turbulence and mixing of the fluids (Kelland 2011; Klomp 2008; Lone 2013), as well as to observe whether the AA can effectively disperse the hydrate phase and allow for continued ball travel throughout the entire test. The key benefit with this equipment is the use of multiple cells placed in one cooling bath, allowing for a multitude of experiments to be tested at a time. This reduces the time required to choose an effective product and define a dosage recommendation.

Specific test conditions, such as rock rate of the cells, cool-down rate, cell hold time and shut-in period are also parameters to be considered and deliberately chosen. Visual observations through-

Fig. 1. Rocking cell equipment.

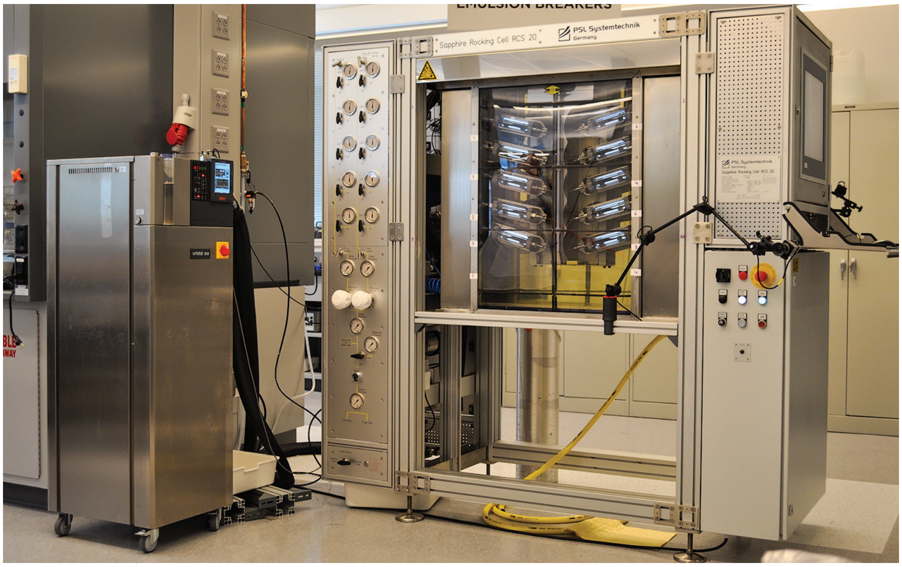


Fig. 2. HEC For field conditions (blue) and for laboratory test conditions (purple).

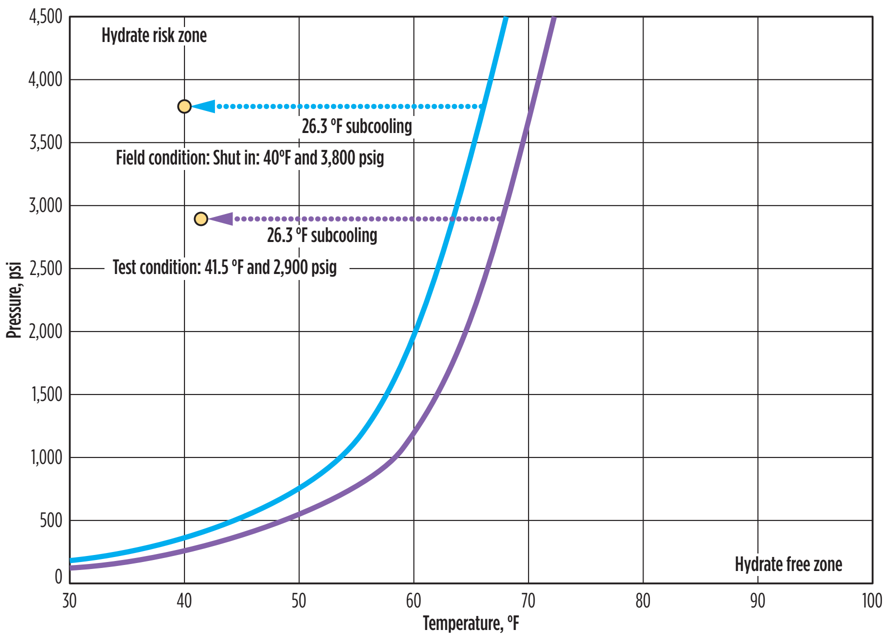


Fig. 3. Autoclave setup.

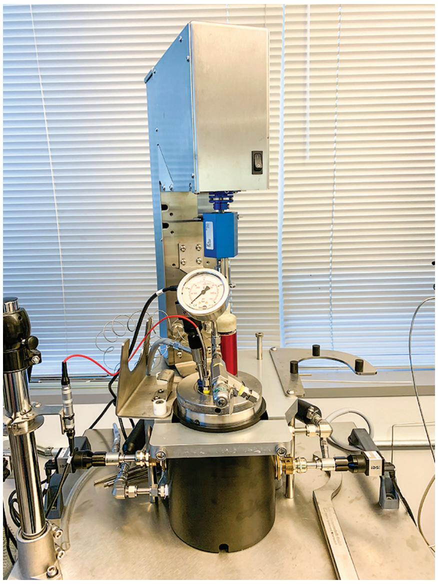
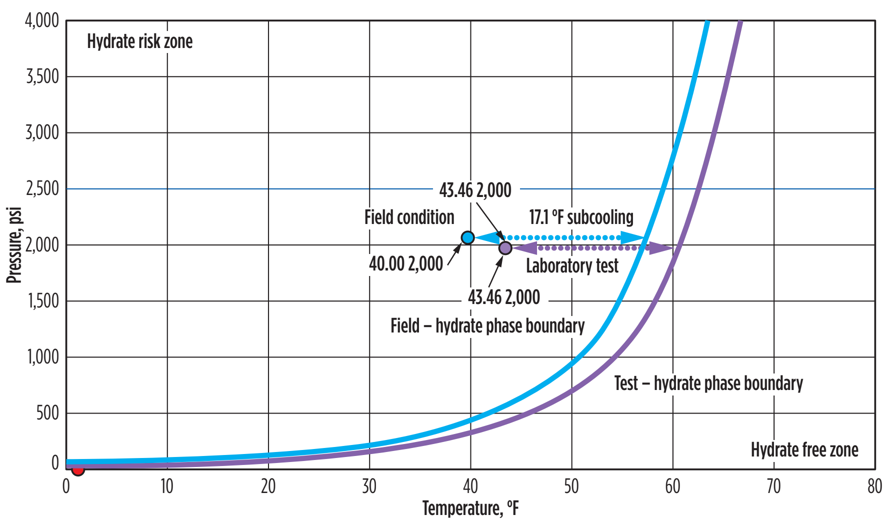


Fig. 4. HEC for field conditions (blue) and for the laboratory test conditions (purple).



out an experiment, especially at critical points, are important to supplement ball travel data. Over the past 10 years, our flow assurance group has improved the internal hydrate testing protocol to better align with field applications. This has been accomplished through laboratory testing, dose rate recommendations, field application and optimization feedback, considering the MED originally recommended and ultimately applied.

Another option for testing is using a stirred high-pressure autoclave. However, there is a limitation in the number of experiments that can be carried out in a given time period and can require significantly more volume of test fluids. This method is preferred when higher shear rates are required, due to higher water cuts and increased volume of hydrates formed.

The extensive experience over many years with LDHI laboratory testing for both rocking cells and autoclaves, as well as successful field applications, was fundamental to improving and optimizing our testing protocols. Understanding the limitations on design and operation of each piece of equipment, and creating a valuable lab-to-field dosage correlation, was also realized through the extensive testing and field observations.

This article highlights the importance of a well-designed testing protocol to simulate field conditions leading to effective treatments. The authors will provide a summary of laboratory test results, using rocking cell and autoclave equipment and the recommended dosages. These recommended AA treatments were implemented and withstood worst case conditions related to shut-ins, followed by successful restart with no indication of hydrate plugging upon resumed production.

EXPERIMENTAL

Rocking cell and autoclave tests were conducted to evaluate the effectiveness of Clariant's **HYTREAT DF 12851A** in two fluids produced from assets located in the Gulf of Mexico (GOM). Rocking cell tests were performed, using Crude Oil A at 30% water cut, and Autoclave tests were performed, using Crude Oil B at 75% water cut. These tests were performed to define the MED for HYTREAT DF 12851A, to prevent hydrate deposition and agglomeration in the flowline in an unplanned shut-in scenario.

Rocking cell test protocol for Crude Oil A. Rocking cell tests were conducted, according to the conditions provided by the operator, considering worst-case scenario for pressure and temperature during a potential unplanned shut-in. **Figure 1** shows the RCS20 rocking cell from PSL Systemtechnik GmbH used to conduct this evaluation.

The general testing protocol applied in this evaluation utilized many variables and conditions, such as rock rate, rock angle, steel ball size, and overall duration of each step. They are test- and field application-dependent, and what constitutes Clariant's experience and expertise. Treatments fail if clear hydrate deposits form during the test and prevent free ball movement from side to side. Treatments pass if the hydrate particles are dispersed effectively into the hydrocarbon phase, and allow for the steel ball to travel unencumbered to each side of the cell when rocked. Observations are also made at key times during the overall test.

Asset A: Hydrate phase equilibrium curve. The gas and brine composition, as well as the key temperature and pressure measurements from Asset A flowline, were provided. Typically, the asset conditions are modeled, then adjusted in the lab to achieve the same subcooling that is experienced in the field. These tests were performed at a 30% water cut, varying the AA dosage from 1.0% to 3.5% by volume water (bvw) in 0.5% increments. As shown in **Fig. 2** and **Table 1,** the testing conditions for this experiment were determined, using a subcooling matching method.

Autoclave test protocol for Crude Oil B. Autoclave tests were conducted according to the conditions provided by the operator, considering a worst-case scenario for pressure and temperature during a potential unplanned shut-in. **Figure 3** shows the autoclave cell PSL Systemtechnik GmbH model GHA 350 used to conduct the evaluation. The testing protocol applied in this evaluation utilized several steps to confirm hydrates are formed and whether they are effectively treated to form a dispersed hydrate slurry. If there are no visual signs of the formation of a gas hydrate plug, or deposits in the autoclave and torque data indicate the free movement of the stir blade, the test is a pass. If torque data suggest a cease in fluid movement, or a lack of proportional torque response to rpm changes, the test is a fail. Additionally, if there is a visual sign of the formation of a gas hydrate deposits or lack of fluid hydrate slurry in the cell, the test is considered a failure.

Asset B: Hydrate phase equilibrium curve. Autoclave tests were conducted, using field conditions provided by the operator from Asset B in a worst-case, unplanned shut-in scenario. These tests were performed at 75% water cut, varying the AA dosage from 0.10% to 0.30% by volume water (bvw) in 0.05% increments, **Fig. 4** and **Table 2.** The gas and

Table 1. Modeling outputs for Asset A and laboratory testing.

Location	Temperature, °F	Pressure, psig	Hydrate temp, °F	Subcooling, °F
Asset A	40.0	3800	66.3	26.3
Rocking cell	41.5	2900	67.8	26.3

Table 2. Modeling outputs for Asset B and laboratory testing.

Location	Temperature, °F	Pressure, psig	Hydrate temp, °F	Subcooling, °F
Asset B	40.0	2000	57.1	17.1
Rocking Cell	43.5	2000	60.6	17.1

Table 3. Rocking cell test matrix with conclusions (2:1 lab-to-field dose rate correlation).

Cell #	Lab dosage, bvw, %	Field dosage, bvw, %	Test conclusion
1-2	Blank	Blank	Fail
3-5	1.00% **HYTREAT DF 12851A**	0.50% **HYTREAT DF 12851A**	Pass
6-8	1.50% **HYTREAT DF 12851A**	0.75% **HYTREAT DF 12851A**	Pass
9-11	2.00% **HYTREAT DF 12851A**	1.00% **HYTREAT DF 12851A**	Pass
12-14	2.50% **HYTREAT DF 12851A**	1.25% **HYTREAT DF 12851A**	Pass
15-17	3.00% **HYTREAT DF 12851A**	1.50% **HYTREAT DF 12851A**	Pass
18-20	3.50% **HYTREAT DF 12851A**	1.75% **HYTREAT DF 12851A**	Pass

Table 4. Autoclave test matrix with conclusions (1:1 lab-to-field dose rate correlation).

Lab dosage, bvw, %	Field dosage, bvw, %	Test conclusion
Blank	Blank	Fail
0.10% **HYTREAT DF 12851A**	0.10% **HYTREAT DF 12851A**	Fail
0.15% **HYTREAT DF 12851A**	0.15% **HYTREAT DF 12851A**	Fail
0.20% **HYTREAT DF 12851A**	0.20% **HYTREAT DF 12851A**	Pass
0.25% **HYTREAT DF 12851A**	0.25% **HYTREAT DF 12851A**	Pass
0.30% **HYTREAT DF 12851A**	0.30% **HYTREAT DF 12851A**	Pass

Fig. 5. Ball travel data for cell treated with 1.0% bvw LDHI.

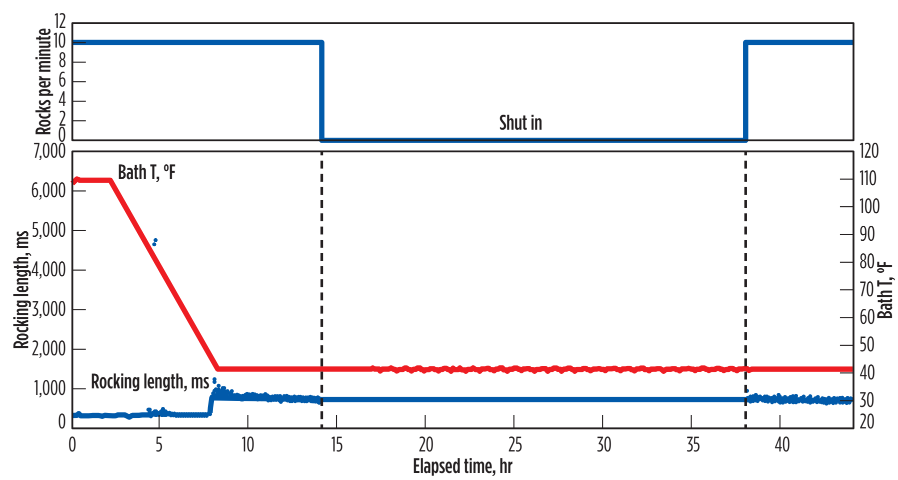


Fig. 6. 1.0% dose during shut-in. No hydrate particles observed.

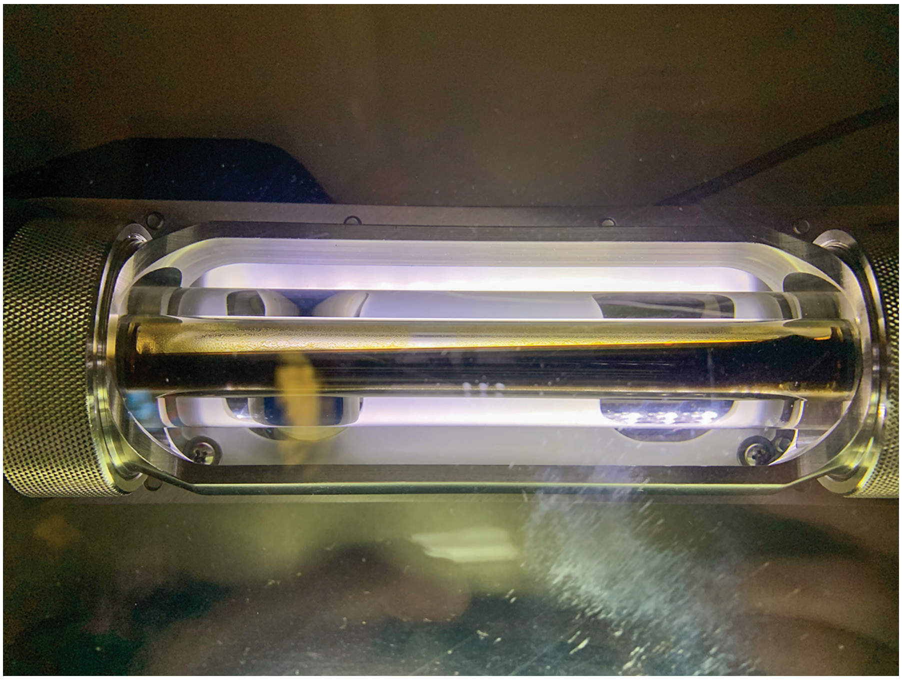
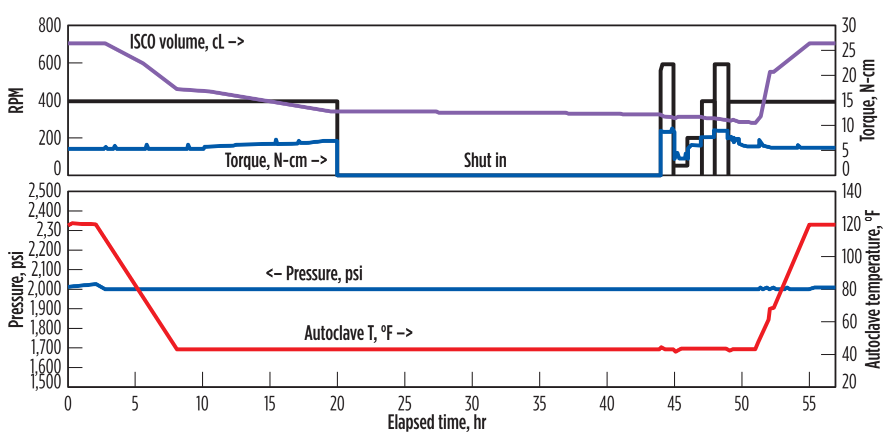


Fig. 7. Pressure, temperature, torque and stirrer RPM for Crude Oil B at 75% water cut treated with 0.20% HYTREAT DF 12851A.



brine composition, as well as key temperature and pressure values from Asset B flowline, were provided and used for subcooling matching. Any differences in the gas composition can be adjusted for within the test condition set-up.

RESULTS AND DISCUSSION

Rocking cell and autoclave tests were performed, using fluids from Asset A and Asset B to evaluate the MED of HYTREAT DF 12851A to mitigate hydrate risk at the given field conditions. For each rocking cell experiment, one or more blank tests are included, to ensure that hydrate plug formation occurs in an untreated condition. Blank testing performed as part of this work showed the expected plugging conditions and resulting fail conclusion.

Results with 1.0% (0.5% field dose) bvw. The following results suggested that a dose rate of 1.0% (lab), based on volume of water (bvw) of AA, was successful at preventing a hydrate plug formation. Hydrate formation is indicated at approximately 8 hours (hr) by an increase in ball travel duration, **Fig. 5.** After 10 hr, ball travel duration remains unchanged, indicating successful dispersion of hydrates through the entire 44-hr experiment. No hydrate plugs or large particles were detected visually, **Fig. 6.**

A laboratory-to-field correlation of 2:1 has been established over the course of 1,000s of laboratory rocking cell tests and dozens of established field applications with this specific chemistry. Laboratory tests presented in this document for Asset A showed an MED of 1.00% bvw at 30% water cut. Field-recommended dosage was, therefore, defined as 0.50% bvw. **Table 3** shows the test matrix performed in this fluid and results for all doses.

Crude Oil B: Autoclave results. The tests for Fluid B were performed using autoclave as the higher water cut for this testing (75%) exceeded the water cut limitations for testing on the rocking cell (typically 50% to 60%). A blank test was included to ensure that hydrate plug formation occurred in an untreated condition and, as expected, resulted in a failure, **Table 4.** Results for 0.20% LDHI at 75% water cut showed a passing slurry behavior with relatively low torque measurements. Hydrate formation started approximately 12 hr into the test, with a peak torque measurement around 5 N·cm. During restart, the fluids did exhibit Newtonian fluid-like behavior, with increasing torque required (shear stress) at increasing stirrer RPM (shear rate). The results were confirmed with visible hydrate slurry in the borescope sight glass. This test was considered a pass. **Figures 7** and **8** depict the torque data and visual results for this test.

LABORATORY-TO-FIELD CORRELATION

This section will correlate the lab dosage recommendation to successful field treatment during shut-in conditions, when applied to operational Asset A and Asset B.

Field A. Successful AA treatment during unplanned shut-in. In Asset A, the deepwater operator in the GOM currently utilizes AA application as part of its flow assurance strategy for three subsea tie-back wells. This application is delivered through umbilical lines, with measured water cut of 16%, but expected to increase to 30% in a relatively short period, thus testing was conducted at the higher water cut.

HYTREAT DF 12851A was determined

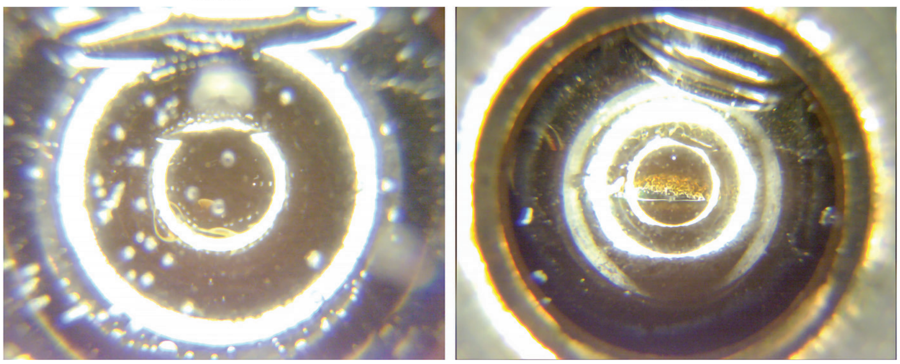
to be effective at 0.50% bvw for a 30% water cut, based on the described testing. However, since the current measured water cut in the field was determined to be 16%, a higher dose rate (1.0%) was suggested to be conservative. Our experience has suggested a 'U'-shaped dosage curve, relative to water cut, actually requires higher dose rates to effectively treat systems at lower water cuts. Our hypothesis, for why this is the case, will be explained in subsequent articles.

During an unplanned shut-in, the production and treatment dosage calculations determined an actual treatment dosage of 0.87% bvw, due to pump speeds and system volumes, in spite of suggested 1.0% bvw. The shut-in occurred for 48 hr, and the system was restarted successfully, with the fluids treated with 0.87% bvw of HYTREAT DF 12851A. This shows the benefit of treating conservatively, to allow for pump variability and production fluid variability.

Field B: Successful AA treatment during planned shut-in. Field B is a single-flowline subsea tieback in a field nearing the end of economic life, due to the cost of hydrate prevention during shut-ins. To address the economic and technical concerns related to treating the field at 75% water cut, testing was requested to verify the feasibility of a lower-dosage treatment with AA to extend economic life. The initial HYREAT DF 12851A dosage rate was 0.30% bvw at 76% water cut. During a planned shut-in of 31 days, the flowline was restarted successfully, with no indication of hydrate deposition or plugging, allowing for continued economic production of the field.

After the well restarted, laboratory tests were performed, with the objective of further optimizing the MED at 75% water cut. Autoclave results indicated a potential optimization in the field dosage to 0.20% bvw HYTREAT DF 12851A, a 33% reduction in applied chemical and associated cost to the operator. After the dosage optimization was applied in the system, the platform was shut-in for seven days, due to a storm. With the recommended dosage of 0.20% bvw of HYTREAT DF 12851A, no hydrate deposits or plugging were observed during the restart process.

Fig. 8. Visual hydrate formation for Crude Oil B at 75% water cut, treated with 0.20% HYTREAT DF 12851A. Start of test with no hydrates (left). After restart with no hydrate deposits (right).



CONCLUSIONS

The lab-to-field correlation of AA dosage treatment was built over years and a wide range of field conditions and fluid compositions. The initial dosage recommendations defined in these tests were applied in field trials in systems flowing in the hydrate region or experiencing risk of hydrate formation during shut-in/restart periods. Taking into consideration the key parameters for each application, we utilized a thoroughly proven protocol for lab testing to arrive at a robust product recommendation for each application.

Results presented also highlight the importance of understanding the design and limitations of the equipment, in order to avoid false negative results. Rocking cell equipment is not designed to handle a high volume of hydrates, due to the shear rate limitation to access the formation of hydrate slurry. The 2:1 ratio dosage defined in the rocking cell has proven to address the conservative approach related to low shear rates, when comparing to the relatively higher shear in the production system. Conversely, a direct correlation of 1:1 is defined when testing the AA in the autoclave, where the shear rates in the tests can reach numbers closer to field, depending on production rates and fluid characteristics.

Recommendations, based on our laboratory testing, have never resulted in any failures in a field application. This highlights our experience and understanding of hydrate risks within production systems, and allows for confidence in our dosage recommendations for worst-case scenarios in the field, specifically for unplanned shut-ins. Many examples beyond the two listed here have proven the success of our treatment recommendations, enabling continued operation, production and income for operators. The success of these applications is a combination of a robust testing protocol, field experience and a high-performance chemical AA. WO

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