



Low Dose Hydrate Inhibitors: a case history of extended shut-in and restart for an anti-agglomerant chemistry in the deep-water Gulf of Mexico and its benefit associated to carbon footprint

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Abstract

Hydrate plugging is a serious flow assurance challenge for deep water production in the Gulf of Mexico (GoM). Operators have a variety of methods to mitigate hydrate plug formation, among which is the use of thermodynamic hydrate inhibitors (THI) and low dose hydrate inhibitors (LDHI) technologies. Often, both technologies are delivered through umbilical lines ranging from 8 to 30 miles in average length, in water depths greater than 6,500 ft. This paper will provide a case study for a specific AA application to prevent hydrate plug formation during an extended field shut-in, fully halting production without the need for flushing the umbilical tubing of AA during shut-in in substitution of regular treatments with methanol, ethanol and monoethylene glycol. The subsea chemicals are all designed to aid in these challenges, while withstanding the harsh injection conditions of the field umbilical delivery system. The risks associated with blocking subsea chemical injection lines can be costly and detrimental to production operations. A rigorous chemical selection associated to the ability to simulate the deep-water conditions in laboratory have aid the operator to successfully proceed with this critical operation and reduce the carbon footprint due to the replacement of regular THI treatments.

Keywords

Low dose hydrate inhibitors; deep water; carbon footprint

Introduction

Hydrate plugging is one of the major concerns regarding technical challenges in an offshore gas production, especially when it comes to deep and ultradeep water operations. Gas hydrates consist of ice-like clathrate solids, with low molecular weight hydrocarbon gases or acidic gases such as carbon dioxide and hydrogen sulfide trapped and floating within these crystal lattice structures. Gas hydrates are formed under conditions of high pressure and low temperature whereby the gases are solubilized by water and become encapsulated in the structure. The lattices are linked together by hydrogen bonding, and if left to grow, can result in blockages and fouling of pipelines, heat exchangers and valves, and can lead to a catastrophic failure of the pipeline. Gas hydrate plugging can stop oil and gas flow, and considering the costs associated with the formation and remediation of gas hydrate plugs, prevention of these blockages is of great importance^{[1] [2]}.

To prevent gas hydrate formation several techniques exist: dehydration, increasing temperature or decreasing pressure, modifications of the gas phase with other gases, and chemical treatments^[3]. At surface, gas dehydration can be realized by using compression, molecular sieves or glycol containing dehydration towers, but this technology is not applicable to subsea wellhead completions. Pipe insulation or heating is an

important method to maintain higher temperatures during normal flowing conditions. Pressure reduction will often remove the hydrate problem, but it is not possible in deepwater.

Chemical inhibitors are frequently applied for the control of hydrate formation. Two inhibitor types are to be distinguished: THIs and LDHIs, which can be further divided into two classes – kinetic hydrate inhibitors (KHI) and anti-agglomerates (AA).

The most relevant THIs used in oil & gas industry are methanol and monoethylene glycol (MEG). Methanol is the most commonly used inhibitor in GoM and West Africa, MEG tends to be used more widely in the North Sea and Asia-Pacific region, while in Brazil, ethanol is the thermodynamic inhibitor of choice due to its wide availability^{[4] [5]}.

AAs allow hydrates to be formed but prevent or delay the agglomeration of the hydrate crystals and subsequently prevent plugging. AAs tolerate subcooling up to 22 °C. In theory, if the dosage is high enough, there might be no limit of subcooling for AAs. Thus, AAs can be applied in deep-water applications, under severe applications even during prolonged shut-in periods. Hydrates that form after an AA treatment will be transportable as a slurry of hydrate particles dispersed in the hydrocarbon phase. To keep the viscosity of the slurry at a level which still allows an easy flow, the water cut shall generally not be higher than 50-60%, even though examples of successful

treatments in fields with water cuts 85-90% exist, e.g. in the Gulf of Mexico^{[1][3]}.

Comparing these two technologies, in terms of its consumption, AAs are effective at 0.5 – 2.0 mass%, whereas THIs are generally used between 10 – 60 mass%, both related to the water phase. Because of this, the AAs are becoming more strategic for oil companies in terms of treatment cost reduction and for being more sustainable compared to THIs.

Methodology

Rocking cell

The approach for designing the rocking cell experiments is to match field conditions as closely as possible. Often, the worst-case scenario regarding temperature and pressure are considered specifically for potential shut-in. Field data and Green Canyon gas composition are reported in Table 1.

Table 1: Gas Composition from field flowline and Green Canyon.

Chemical Symbol	Field Gas (mol %)	Green Canyon Gas (mol%)
N ₂	0.16	0.14
CO ₂	0.14	0.00
H ₂ S	95.24	0.00
C1	1.44	87.56
C2	1.49	7.60
C3	0.22	3.00
i-C4	0.62	0.50
n-C4	0.17	0.80
i-C5	0.21	0.20
n-C5	0.13	0.20
C6	0.17	0.00
C7+	0.00	0.00

Temperatures usually approximates to the sea floor temperatures (~39°F) and many times operating pressures increase upon shut in.

Fill the cells (20 mL total volume) with representative crude oil, test brine, and the LDHI-AA with ranging from 0 – 2%. Evacuate the cells with a vacuum pump for the duration of 15-20 minutes, then pressurize them with the test Green Canyon (Table 1) to the pressure of 2,900 psi.

Start rocking the cells at the rate of 10 rocks per minute and increase the bath temperature to 120°F. Once the bath reaches that temperature, keep rocking the cells for 2 hours or until no further gas is consumed and fluids have been saturated and reached equilibrium. While rocking the cells at the rate of 10 rocks per minute, cool down the system from 120°F to 43.5°F over 4 hours (Table 2). For Static Shut-in Simulation test, rocking is

stopped after the saturation step prior to cooling down.

At the constant temperature of 43.5°F, keep rocking the cells at the rate of 10 rocks per minute for 12 hours to ensure complete hydrate formation. Then, stop rocking, set the cells to a horizontal position and keep the temperature constant at 43.5°F for 24 hours minimum.

Start rocking again at the rate of 10 rocks per minute at the constant temperature for 12 hours. Capture video and pictures within 10 minutes after restart. While rocking the cells at the rate of 10 rocks per minute, heat the system from 43.5°F to 120°F over 4 hours.

Table 2: Summary of field and lab test conditions.

Location	Temperature (°F)	Pressure (psig)
Field	40.0	2,000
Rocking cell	43.5	2,0300

*Field and Rocking cell sub-cooling are 35°F.

Product Carbon Footprint

Product carbon footprint (PCF) is based on the global warming potential using characterization factors from the Intergovernmental Panel on Climate Change Assessment Report 5 (IPCC AR5) with a 100-year timeframe. The final result is expressed as kg CO₂ equivalents per kg of product. The GaBi Software has been used as well as its database, where possible. The data set covers all relevant process steps/technologies over the supply chain of the represented cradle to gate inventory.

Results and Discussion

Rocking Cell

For each rocking cell experiment, one or more blank tests are included to ensure that hydrate plug formation occurs in an untreated condition. In this experiment, cells 1 and 2 were left untreated. Both cells finished the experiment indicating clear evidence of hydrate plug formation both visually and through ball travel measurement. Hydrate plug formation occurred at approximately 8 hours, suspending ball travel.

The results suggested that a dose rate of 0,5% based on volume of water (bv_w) of LDHI was successful at preventing a hydrate plug formation. Hydrate formation is indicated at approximately 8 hours by an increase in ball travel duration (Figure 1). After 10 hours, ball travel duration remains unchanged, indicating successful dispersion of hydrates through the entire 44 hour experiment. No hydrates were detected visually.

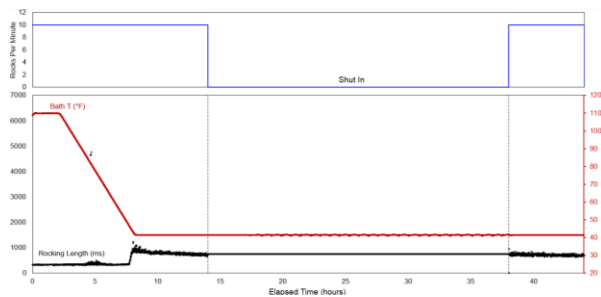


Figure 1. Graph Measuring Ball Travel Data for 0.5% of LDHI-AA.

Laboratory-to-field correlation

This section correlates the field successful treatment during shut-in conditions when applying initial recommended dosages according to laboratory testing protocol and field trial results.

In the Field, the deepwater operator in the GoM currently utilizes LDHI application as part of its flow assurance strategy for 3 subsea tie-back wells. This application is delivered through umbilical line ranging from 8 to 21 miles long, in water depths greater than 6500 ft.

Rocking cell tests were performed with 30% water cut with an initial LDHI recommended field dosage of 0.50% bvwt. Because the initial tests were performed with 30% water cut and water production rates were approximately half of this volume (measured at 16%), based on previous experience the recommended LDHI dosage at this rate was 1.00% bvwt. During an unplanned shut-in the production and treatment dosage calculations determined an actual LDHI dosage of 0.87% bvwt. The shut-in occurred for 48 hours and the system was successfully restarted the fluids treated with 0.87% bvwt.

The lab-to-field correlation of LDHI dosage treatment was built over the years in a wide range field conditions and fluid compositions. The initial dosage recommendations defined in these tests were applied in field trials in systems flowing under hydrate region or experiencing critical risk of hydrate formation during shut-in/restart periods.

These applications allowed creating a lab-to-field correlation for the LDHI with an indication of a well-designed testing protocol taking into consideration the key parameters required to accurately recommend a successful hydrate management strategy.

Figure 2 shows the field parameters reached during trial with LDHI-AA. Replacing MeOH completely with LDHI-AA reduced the THI volume from an average of 1,450 GPD to less than 400 GPD of the new chemical. This represented a saving in storage in the platform and costs related to logistics. Also, carbon emission was reduced by the application of this solution, requiring less frequent chemical deliveries via boat, reaching at least a reduction of 58% of carbon emission due to less chemical consumption during this operation.

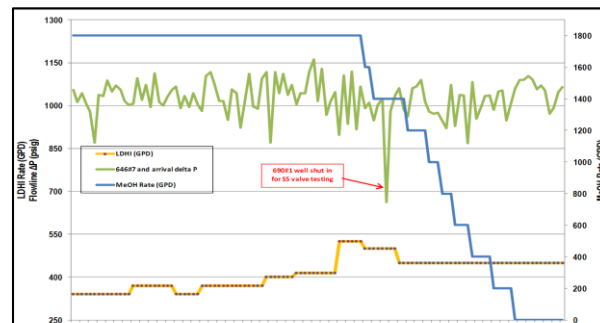


Figure 2: LDHI-AA versus Methanol consumption in the field.

Conclusions

Results presented also highlighted the importance of understanding the design and limitations of the equipment in order to avoid a false negative result related to the performance of the chemistry.

By maintaining injectivity, the operator from Field was able to minimize production time loss during restart by not flushing the umbilical during the planned shut-ins. This decision was made based on LDHI lab-to-field tests that promoted a reduction of treatment cost and carbon footprint by 85% and 58%, respectively compared to methanol.

Responsibility Notice

The authors are the only responsible for the paper content.

References

- [1] Miller, R.; Sim, M.; Kelly, C.; Bodnar, S.; Wylde, J. Current Advantages and Limitations of Low Dose Hydrate Inhibitors in Subsea Flow Assurance and Considerations for Future Optimisation. Oil Field Chemistry Symposium, Geilo, Norway, 2016
- [2] Y., J. H. . A. I. . L. J. . K. I. Prevention of hydrate plugging by kinetic inhibitor in subsea flowline considering the system availability of offshore gas platform. Journal of Industrial and Engineering Chemistry, v. 82, p. 349–358, 2020
- [3] KELLAND, M. A.; History of the development of Low Dosage Hydrate Inhibitors, Energy and Fuels, 20, 825 -846, 2006
- [4] Anderson, R., Chapoy, A., Tanchawanich, J., Haghghi, H., Lachwa-Langa, J. and Tohidi, B., Binary Ethanol-Methane Clathrate Hydrate Formation in the System CH₄-C₂H₅OH-H₂O: Experimental Data and Thermodynamic Modelling, 6th International Conference on Gas Hydrates (ICGH). Vancouver, British Columbia, CANADA, 6-10 July, 2008
- [5] Mazloum, S.; Yang, J.; Chapoy, A.; Tohidi, B.; A Novel Technique for Optimising Hydrate Inhibitor Injection Rates. Offshore Technology Conference Brasil, Rio de Janeiro, Brazil, 2011.