A New Approach to Evaluate KHI Performance

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ABSTRACT

The Karan field is Saudi Aramco's first offshore nonassociated gas, which started production in mid-2011. The gas is sour (2% H_2S and 8% CO_2) and lean with no hydrocarbon condensate. The gas is predicted to produce 2 bbl/mmscf of condensed water with 750 ppm of organic acids. Condensation of water creates a high risk for both corrosion and gas hydrates during winter.

As such, there is a great challenge to find a suitable and compatible Kinetic Hydrate Inhibitor (KHI) in the presence of a Corrosion Inhibitor (CI) for a predominantly Hydrate Structure I system. Saudi Aramco approached Hydrafact Ltd (a Heriot-Watt University spin-out company), which offered a new technique for evaluating KHI performance and has considerable knowledge of KHI inhibition mechanisms.

This paper describes the work that has been done to independently evaluate KHI performance for the Karan field. The work involves evaluation of various mixture KHI and CI at different concentrations for the Karan system, using crystal growth inhibition (CGI) and traditional induction time methods with test protocols for the latter specified by Saudi Aramco. In addition, the effect of corrosion inhibitor on KHI performance was also analyzed. The performance of two different KHIs was also compared. The work done has increased Saudi Aramco confidence and understanding of hydrate inhibition using KHI.

Keywords: gas hydrates, kinetic inhibitors, sour gas production

NOMENCLATURE

ΔTs-I	Temperature difference from s-I hydrate phase boundary [°C]
ΔTs-II	Temperature difference from s-II hydrate phase boundary [°C]
bbl	barrel (42 U.S. gallons)
BCI	Batch Corrosion Inhibitor
BIC	Best in Class
CAPEX	capital expenditures
CCI	Continuous Corrosion Inhibitor
CI	Corrosion Inhibitor
CIR	Complete (hydrate) Inhibition Region
CGI	Crystal Growth Inhibition
gpm	U.S. Gallons per minute
KHI	Kinetic Hydrate Inhibitor
LDHI	Low Dosage Hydrate Inhibitor
MeOH	Methanol
MEG	Mono Ethylene Glycol
MMscfd	Million standard cubic feet per day
mg/L	milligram per liter
mpy	milli-inch per year
NGL	Natural Gas Liquids
OPEX	operating expenditures
psig	pounds per square inch (gauge)
ppm	parts per million
PVCap	Polyvinylcaprolactum
RGR	Rapid (KHI) Growth Region
SGR	Slow (hydrate) Growth Region
SDR	Slow (abnormally, hydrate) Dissociation Region
TDS	Total dissolved solids
TEG	Tri-Ethylene Glycol
TP	Tie-in Platform
t_i	Hydrate nucleation induction time [hrs]
”	inch = 2.54 cm
WHP	Wellhead Platform

INTRODUCTION

Formation of hydrates poses a serious concern in gas production in general and especially for offshore gas production where gas is transported in long trunk lines. Hydrates are often encountered within subsea pipelines carrying wet gases in cold winter operation. The conventional chemical treatments to prevent hydrate formation are thermodynamic inhibitors such as monoethylene glycol (MEG) and methanol (MeOH). They are classified as “thermodynamic” inhibitors because they are able to shift the hydrate equilibrium curve toward higher pressures and lower temperatures by changing the activity of the water molecules [1]. It is known that the CAPEX and OPEX cost associated with thermodynamic inhibitors can be prohibitively expensive [2]. Low Dosage Hydrate Inhibitors (LDHIs) such as Kinetic Hydrate Inhibitors (KHIs) were then successfully deployed as they offer significant cost savings advantages over thermodynamic inhibitors.

KHI application for sour lean gas fields is still limited as this type of gas tends to form Hydrate structure I which makes the KHI qualification more challenging compared to gases with structure II hydrates [3]. Thus, qualifying the KHI requires additional evaluation beyond the traditional induction time methods to ensure that the qualified KHI will perform well in such an environment.

This paper describes the work done to independently evaluate the KHI-based hydrate inhibition strategy for a sour gas field. The work involves evaluating various KHI and CI mixtures at different concentrations using the novel Crystal Growth Inhibition (CGI) method developed by Hydrafact. The work conducted in this project increased Saudi Aramco’s confidence with the KHI being selected to be used for this application.

BACKGROUND

Saudi Aramco entered a new territory in 2011 by producing nonassociated gas from its first offshore gas field. The field produces sour wet gas with 2% H_2S, 8.5% CO_2 and 2 bbl/mmscf of condensed water. The gas is lean with no hydrocarbon condensate as only water condenses throughout the pipeline mainly due to the Joule Thompson (J-T) cooling effect. Water condensation and temperature drop is more severe during winter. Condensation of water within the pipeline leads to the requirement of effective corrosion and hydrate control measurements.

To address both the corrosion and hydrate concerns, chemical inhibition in combination with internal coating has been considered. A rigorous and extensive chemical compatibility test protocol was developed to select the right combination of chemicals to be used. The maximum sub-cooling requirement is 10.5ºC at the gas plant. This is considerably high thus it was determined that KHI would be used for offshore protection and supplemented with MEG for onshore protection. This means for offshore protection the required sub-cooling protection is up to 5.6ºC. Due to the feed gas composition which requires high CI concentration and hydrate structure I, there was a challenge to qualify a KHI that can survive high concentration of CI at the required sub-cooling of 5.6ºC.

Thus, based on KHI and CI compatibility test findings during the qualification testing [4] where the KHI vendor(s) barely passed the traditional induction/hold time method protocol test, Saudi Aramco decided to perform an independent KHI testing to independently evaluate the design of the KHI-based hydrate inhibition strategy for the pipeline system using a new technique for evaluating KHIs.

All the tests were conducted at Hydrafact. This alternative test approach provides robust, repeatable and transferable KHI data. Furthermore, it increases the operator confidence in KHI performance as it improves the understanding of KHI inhibition mechanism [7].

STUDY OBJECTIVES

The main objectives of the study were:

a. Review previous KHI experimental test data from the approved vendor.
b. Experimentally determine equilibrium hydrate dissociation conditions for the test gas mixture and compare with model predictions/previous experimental data.
c. Evaluate the proposed KHI (+CI) at different concentrations for the system using CGI method and compare with traditional induction time method with test protocols for the latter specified by Saudi Aramco.
d. Evaluate the effect of corrosion inhibitor on KHI performance and whether reducing the CI concentration could extend KHI working sub-cooling range.
e. Determine potential alternative KHIs.
f. Evaluate the effect of MEG on KHI performance and whether it could be used in combination with the KHI inhibition for hydrate inhibition, particularly with respect to the onshore section, which experiences a higher sub-cooling.
g. Evaluate the effect of salt (saline water) on KHI performance.
h. Calculate the dose of MEG needed for thermodynamic hydrate inhibition (no KHI) under winter low flow rate conditions.
i. Assess cloud point and polymer deposition potential for aqueous KHI solutions as a function of temperature with and without corrosion inhibitor present.

SCOPE OF STUDY

The study scope involved 2 stages:

Stage 1 – This stage covered objectives "a-e." Hydrate inhibition performance for various KHI and CI inhibitors mixtures at different concentrations using CGI [5, 6] and traditional induction time methods were evaluated. In addition, the effect of CI on the KHI performance was analyzed. To pass a KHI, the test protocol requires no signs of hydrate formation during the first 144 hours of the test at the required degrees of sub-cooling.

Stage 2 – This stage covered objectives f-i. The work in this stage determined the effect of thermodynamic inhibitors, salt or saline water on the hydrate inhibition performance of KHI.

This paper will only present findings related to Stage 1 to demonstrate that CGI is an effective method to evaluate KHI hydrate inhibition performance.

RESULTS AND DISCUSSION

The results for the various objectives are discussed below:

a) Review previous KHI experimental test data for the approved vendor.

The analyses from the original qualification tests results were consistent with CGI regions. Likewise Hydrafact performed induction time tests that yielded the required induction times for the sub-cooling condition.

Thus it is concluded that the data of the previous work are generally consistent with each other and that apparent observed discrepancies between these two sets of independent tests are likely the result of the following:

- Inherent stochasticity in hydrate induction times. Induction time methods are inherently stochastic, particularly at low sub-cooling and can be quite sensitive to experimental design.

b) Test gas hydrate dissociation conditions.

During the model validation process, equilibrium hydrate dissociation conditions have been measured for the test gas (Table 1) using a constant volume isochoric equilibrium step-heating technique. This is important to be verified as small deviations in the gas composition and/or water/gas ratio may result in changes in the hydrate stability zone, hence degree of subcooling.

Measured dissociation conditions are consistent with previous findings. As shown in Figure 1, three hydrate dissociation points were observed, with the final hydrate dissociation point corresponding to the most stable H_2S-rich Structure I hydrate, as predicted by the HydraFLASH® model. It should be noted that the changes in structure observed in tests as a function of hydrate fraction is the result of the system being constant volume/gas limited. In the pipeline, the more stable structure is hydrate structure I, although structure II could theoretically form at temperatures lower/pressures higher than the structure II boundary shown in Figure 1.

c) KHI performance: effect of KHI concentration.

During the initial KHI/CI qualification test, there were some conflicting results obtained from the vendor and an independent third party test facility whether the combined chemical can meet the 5.6 ºC sub-cooling at the required pressure.

With the alternative CGI test approach, it became easier to understand the results in a more objective manner and in more depth at various sub-cooling conditions.

The reader should refer to Table 2 for an explanation of regions and relative hydrate growth rates within these.

As can be seen from Figures 2-3, at a sub-cooling of 4°C, 2.5% and 3.0 vol% KHI indicated very slow or complete inhibition of crystal growth across the pressure range of interest. This observation is consistent with the extended induction times generally observed at these conditions.

At a sub-cooling of 5.0°C, only 3.0%vol KHI shows reduced growth or very slow growth, with 2.5%vol showing moderate growth rates while 2.0%vol shows moderate growth rates.

At 5.6°C sub-cooling, only 3.0%vol KHI shows good crystal growth inhibition, moderate to rapid growth conditions applying for both 2.0 and 2.5%vol KHI across the pressure range of interest for both these concentrations.

To compare with the CGI method findings, tests were also replicated with the original induction time protocol as used during the qualification test.

Tests were carried out on 2.5 and 3.0% KHI with 2000 ppm CI. In addition to this, induction times using the new protocol specified by Saudi Aramco were carried out on 2.0, 2.5 and 3.0% KHI with 2000 ppm CI. Results are reported alongside with previous test results in Table 3. The tests were done at two pressure conditions: 100 bar, which is based on a shut-in condition while 70 bar is based on a flowing condition.

Results using the original test procedure are consistent with the previous test; at both KHI concentrations, an induction time of greater than 144 hours was observed. On further cooling to 5.6 °C, hydrate growth began in the system with 3.0%vol KHI within 1 hour. For 2.5%vol KHI, the experiment was terminated as hydrate formed almost immediately after the temperature of the cell was changed, indicating a high degree of nucleation sensitivity to environment at this condition, which is consistent with CGI region conditions.

d) KHI Performance: Effect of corrosion inhibitor concentration.

From the initial qualification tests, it was confirmed that CI concentration above 2000 ppm will have an adverse impact to KHI performance. It was not clear how will the KHI perform if the CI concentration goes lower. For the purpose of the test, it was decided to see if there is any hydrate inhibition improvement when the CI concentration was reduced to lower than 2000 ppm and down to 1250 ppm (which is an assumed value taken for acceptable corrosion inhibition performance).

This was tested using CGI methods for 2.5 and 3.0 vol% KHI for comparison with data already generated for 2000 ppm CI, to see if any improvement in KHI performance could be observed.

Figure 2 shows a comparison of determined CGI region boundary sub-cooling for both KHI concentrations at 2000 and 1250 ppm CI levels. As can be seen, reducing the CI concentration from 2000 to 1250 had no clear detectable effect on KHI performance at both KHI doses within experimental error; CGI regions remaining largely identical at both CI levels. This supports the findings that the CI is compatible with KHI (at least in terms of KHI performance), but reducing the CI concentration is not apparently improving the KHI performance.

e) Alternative KHI potential

Further tests were conducted to determine whether there was a potential for finding an alternative, better formulation than the approved KHI from the qualification tests.

Tests were conducted on a generic carrier (20 wt% PVCap polymer/80 wt% MEG solvent) and two alternative KHIs available in the market; the latter two being supplied in the past for other field evaluation studies. Figure 3 shows determined CGI region boundary sub-coolings for all three, compared with those for the original KHI.

As can be seen from Figures 3, for the conditions tested:

- The existing KHI showed better performance than a simple PVCap-MEG mixture.
- Alternative-A KHI showed poorer performance than the existing KHI.
- Alternative-B KHI showed better performance than the existing KHI, with hydrate growth completely inhibited (CIR green zone) at the 4°C sub-cooling, i.e., the condition envisaged for long shut-in periods.

The better performance of Alternative-B KHI suggests that there was scope for finding (or formulating) a KHI that could offer suitable performance at 2.5 vol%, even for long shut-in conditions; at least at lower sub-coolings. It should be noted that no CI was used in the tests; therefore the test results were not yet conclusive, and further testing in the presence of CI was required.

Alternative-B KHI vendor was subsequently approached to provide a commercially available KHI/CI package for this application. Their package was tested using CGI method and the results (refer Vendor 2 in Figure 4 for generic comparison), suggested that the new reformulated KHI/CI package is able to exceed the required hydrate inhibition performance achieved by Vendor 1. This provided confidence for Saudi Aramco to pursue qualification for the alternative KHI/CI package to be used for this application.

SUMMARY OF ANALYSIS

The findings for the work conducted in this project could be summarized as:

i. KHI (with 2000 ppm continuous CI) induction time results are consistent with the qualification test results conducted at a third party laboratory. This essentially verified the results obtained from the qualification tests. Any apparent discrepancy between the latter two being likely the result of differing experimental apparatus and/or the inherent stochasticity associated with hydrate nucleation in the traditional induction time method

ii. Using the CGI method, it is demonstrated that the hydrate growth rate patterns as a function of sub-cooling in the original experimental data are consistent with CGI regions for KHI+CI systems measured as part of this work, supporting the above conclusions. This provided the confidence required that the qualified KHI would work as expected for the sour lean gas composition in this field.

iii. The recommended concentration based on the original qualification tests suggested a minimum of 2.5%vol for KHI with 2000 ppmv CI dosage rate. Based on Hydrafact's induction time measurements and CGI data, 3.0%vol KHI provides consistently good performance, up to 5.6 °C sub-cooling with 2000 ppm CI. 2.5%vol is borderline and while potentially sufficient at least for 4 °C sub-cooling; its performance during shut-in is questionable and results in hydrate formation risks.

iv. The tests showed that the CI is compatible with KHI, which is consistent with the original qualification test results. KHI performance was affected negatively by CI concentrations higher than 2000 ppm; however reducing the CI concentration from 2000 ppm to 1250 ppm did not improve KHI performance.

v. Tests on a basic KHI formulation comprised of 20 wt% PVCap polymer/80% wt% MEG dosed at 2.5 vol% aqueous (LTDS brine), showed that this formulation performed more poorly than Karan qualified KHI. The same was found for another, randomly selected KHI formulation.

vi. A randomly selected KHI from a different vendor performed better than the Karan qualified KHI, suggesting a potential for finding a commercial KHI with better performance for the sour lean gas. CGI test data comparison with the existing KHI confirmed that the reformulated KHI/CI package from the new vendor exceeded the required hydrate inhibition performance.

CONCLUSION

Hydrate management assessment for Karan gas field provided the necessary experience to conclude that due to the feed gas composition, which requires high CI concentrations and results in predominately structure-I hydrates, there was a challenge to find the required KHI.

Thus, Saudi Aramco approached Hydrafact to independently re-evaluate the performance of its qualified KHIs using the CGI method. This novel method developed by Hydrafact provided an alternative assessment to the qualified KHI in sour lean gas production field application.

The CGI tests demonstrated that the results are consistent with the traditional induction time method performed for the qualification tests. In addition, it provided a better understanding on the ranges of KHI/CI concentration to be used at flowing and shut-in conditions. The CGI testing procedure also allowed for immediate screening of a new KHI/CI package; permitting to identifying a particular chemical package with promising results. The CGI tests also increased Saudi Aramco confidence with the qualified KHI.

The experience gained from the independent tests to manage hydrate inhibition for a sour lean gas production field have provided the company with invaluable knowledge, in optimizing the existing offshore gas production chemical dosage rate and developing new strategies for future fields. The tests allowed Aramco to qualify a second KHI chemical vendor, to allow for better product competition with the existing qualified vendor.

FIGURES AND TABLES

The results for the various objectives are discussed below:

Component	Mole%
C_1	79.6
C_2	1.4
C_3	0.2
n-C_4	0.1
CO_2	9.2
H_2S	2.3
N_2	7.2

Table 1. Sour lean gas field gas properties

	Typical growth rates order of magnitude (% water / hr)	Growth rate Description
CIR	0.00	No growth
SGR (VS)	0.01 (< 0.05)	Very slow
(S)	0.1 (≥ 0.05 to < 0.5)	Slow
(M)	1 (≥ 0.5 to < 5)	Medium
RGR	10 (≥ 5)	Rapid
SDR	Dissociation rate one order of magnitude less than for no KHI	(Abnormally) Slow dissociation

Table 2. Classification of CGI regions based on orders of magnitude change in hydrate growth rates (% water converted to hydrate per hour) as commonly observed across region boundaries. Defining characteristics of the hydrate slow dissociation region (SDR).

Pressure	KHI	Test No.	t_i 1	t_i 2	t_i 3	t_i 4	Min t_i @ 5.6°C ΔT_{sub}
			#t_i @ 4.0°C ΔT_{sub}				
~100 bar	2.0% Conc.	Test 1	116.0	131.0	133.0	>145.5	116.0
	2.5% Conc.	Test 2	122.5	145.5	145.1	145.1	1.5
		Hydrafact Karan 01	144.0	-	-	-	>85.0
	3.0% Conc.	Test 3	41.5	145.0	145.0	145.0	41.5
		Test 4	144.0	144.0	144.0	144.0	>24.0
		Hydrafact Karan 02	144.0	-	-	-	1.0
			t_i @ ΔT_{sub}				
			*4.0	5.0	5.6		
~70 bar	2.0% Conc.	Hydrafact Karan 03	120.0	24.0	47.0		
	2.5% Conc.	Hydrafact Karan 04	74.0	-	-		
	3.0% Conc.	Hydrafact Karan 05	120.0	24.0	>115		

#Original procedure

*New procedure (24 hours flowing, 72 hours shut-in, 24 hours flowing at 4 °C subcooling)

Table 3. Experimental induction time data for the system for various concentrations of KHI (with 2000 ppm corrosion inhibitor) at pressures of 100 bar (original procedure) and ~70 bar (new procedure). Induction times are colored according to appropriate CGI region conditions

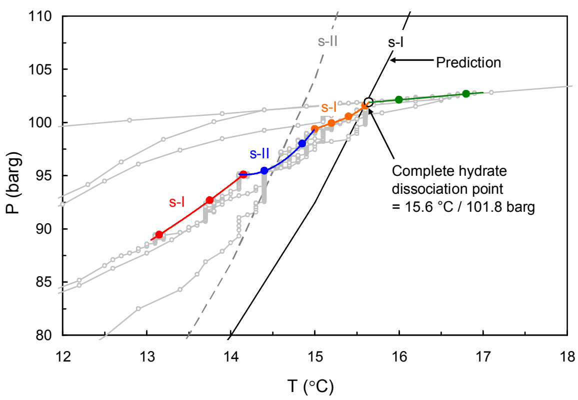

Figure 1. Determined hydrate equilibrium points and interpolation for gas hydrate conditions compared with HydraFLASH® model predictions

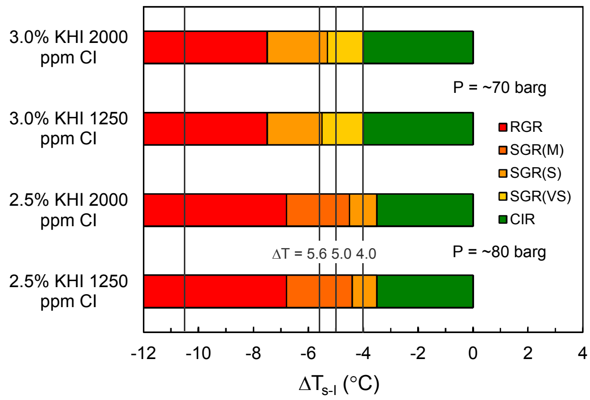

Figure 2. Comparison of determined CGI region boundary sub-coolings for 2.5 and 3.0 vol% at 2000 and 1250 ppm CI concentrations.

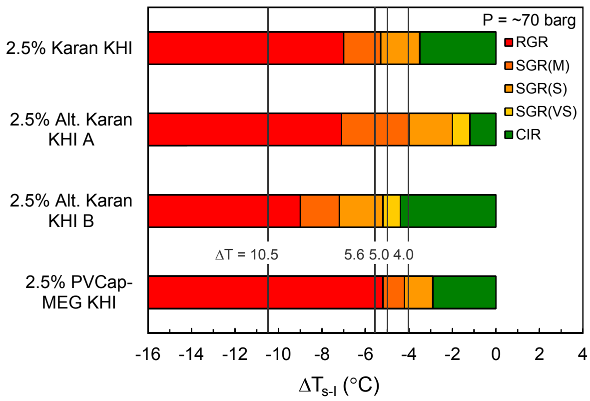

Figure 3. Comparison of determined CGI region boundary sub-coolings for various KHIs'.

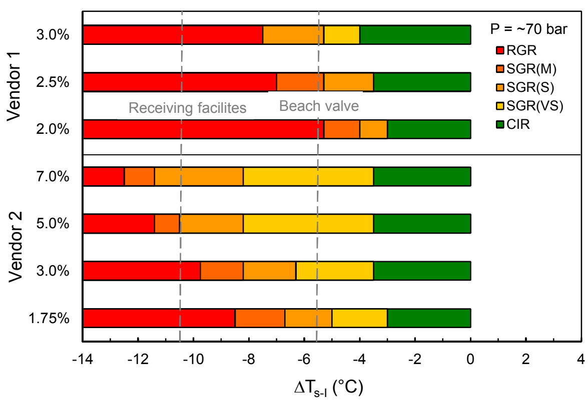

Figure 4. Comparison outline of determined CGI region boundary sub-cooling for the two KHI/CI chemical packages

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