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DEVELOPMENT OF EFFECTIVE COMBINED KINETIC HYDRATE INHIBITOR / CORROSION INHIBITOR (KHI/CI) PRODUCTS

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ABSTRACT

Low Dosage Hydrate Inhibitors (LDHIs) are gaining worldwide acceptance as a viable alternative to the more conventional methods of hydrate flow assurance control. Use of this LDHI technology in combination with Corrosion Inhibitors (CI) in production systems such as subsea developments enables operating companies to further significantly reduce capital costs.

CI can have a significant impact of the efficacy of Kinetic Hydrate Inhibitors (KHI). This paper will review the experience of developing combined KHI and CI products (KHI/CI) with the aim of producing effective products whilst also incorporating the goal of the use of more environmentally friendly CI. Relevant KHI/CI product case histories will be considered. The development of KHI to be used in the presence of CI will also be considered in different production scenarios. This relates to the typical situation of continuous CI usage with the seasonal application of KHI. Experience is also shown of how the incorporation of Thermodynamic Hydrate Inhibitors (THI) to KHI/CI products, in order to enable the combined product to control hydrates in higher subcooling systems, can also have a role to play in the influence that the CI has on the efficiency of the KHI.

Keywords: Kinetic Hydrate Inhibitor, Corrosion Inhibitor, Effective combined products

NOMENCLATURE

The following abbreviations and acronyms are used throughout the text:

AA	Anti-Agglomerant hydrate inhibitor
Bbl	Barrel (42 US Gallons = 0.159 m^3)
Bcpd	Barrels of condensate per day
Bopd	Barrels of oil per day
Bpd	Barrels per day
Bwpd	Barrels of water per day
CI	Corrosion Inhibitor
“	Inch = 2.54 cm
KHI	Kinetic Hydrate Inhibitor

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LDHI	Low Dosage Hydrate Inhibitor
MEG	Ethylene Glycol
MeOH	Methanol
MM	Million
MMscf	Million standard cubic feet
MMscfd	Million standard cubic feet per day
mpy	mils per year (corrosion rate)
p	Pressure
Psi	Pounds per square inch
T	Temperature
THI	Thermodynamic Hydrate Inhibitor

INTRODUCTION

The inhibition of gas hydrate formation and the separate issue of the prevention of corrosion are two important considerations that need to be taken into account as part of the production of oil and gas. Gas hydrates form when natural gas molecules are surrounded by water molecules to form 'cage'-like structures. Gas hydrates are crystalline structures that look similar in appearance to ice and have similar characteristics – with the difference that hydrates incorporate a natural gas guest molecule as part of the structure [1-4]. Typical hydrate forming gases include light hydrocarbons (methane to heptanes), Nitrogen, Carbon Dioxide and Hydrogen Sulfide. Hydrates typically form at lower temperatures and higher pressures. Depending on the gas composition and the pressure, gas hydrates can form at temperatures of up to 18°C where gas co-exists with water [5-6]. Production facilities, particularly offshore wells and offshore transmission lines, may be operating under conditions where hydrate formation is favourable. Gas fields typically require continuous hydrate protection from the beginning of their life cycle. This is required as the hot gas being produced cools as it flows from the well via an uninsulated subsea line - leading to the formation of condensate and water. Oil wells on the other hand may only start producing water a couple of years into their life cycle. From that point onwards they will require protection from hydrate formation.

Hydrate inhibition and control is an important part of the design and operation of offshore production systems in order to prevent the formation of hydrate blockages [7]. Hydrate plug formation and subsequent remediation can be a costly occurrence. Hydrate plugs may take days to months to dissociate depending on the system conditions and the remediation actions taken. This is costly in terms of deferred production. The action of trying to locate a blockage (particularly in an offshore production system) is also difficult. Remediation options include depressurization and/or the application of MeOH or MEG to help melt a hydrate plug. Other options include trying to apply heat to help speed up the melting of a hydrate plug. All options need to be carefully considered to minimize the risks involved, such as the liberation of significant quantities of gas in a short time frame from a hydrate plug if heat is applied to the hydrate blockage.

In the prevention of hydrate formation several options are available to operating companies. Thermal insulation may be used to reduce heat loss from subsea pipelines to their colder surroundings – such that operating conditions are warmer and less likely to lead to hydrate formation. Another option is to dehydrate offshore production fluids before they are transported – leading to the requirement of offshore dehydration process units. Both of these options require significant additional capital expenditure (CAPEX). Another option is that production pressure could be decreased to reduce the likelihood of hydrate formation. However, this has the associated costs of deferred production. Chemical additives to the production fluids are another option that may be considered and are discussed in further detail below.

The protection of production assets from the effects of corrosion is also an important process for oil and gas producers. Corrosion is the oxidation of iron via the formation of an electrochemical cell under appropriate conditions, such as when oxygen rich water is in contact with an iron surface. Detection, monitoring and control of corrosion in oil and gas production systems are important considerations. Corrosion control engineering practices are common throughout the oil and gas industry [8] and these include the application of chemical corrosion inhibitors.

LOW DOSAGE HYDRATE INHIBITORS

Chemical additives that could be used for hydrate inhibition can generally be divided into three categories;

1. Thermodynamic Hydrate Inhibitors,
2. Kinetic Hydrate Inhibitors (KHI), and
3. Anti-Agglomerants (AA).

Both KHIs and AAs fall into the category of Low Dosage Hydrate Inhibitors.

The Thermodynamic Hydrate Inhibitors lower the formation temperature of hydrates by approximately the same amount as they lower the freezing point of ice [9]. This is because gas hydrate structures consist of hydrogen bonded water molecules as is found in ice. The Thermodynamic Hydrate Inhibitors compete with the water molecules in terms of hydrogen bonding – making the formation of hydrates thermodynamically less likely. Thermodynamic Hydrate Inhibitors include salts, methanol and glycols such as ethylene glycol. However, the Thermodynamic Hydrate Inhibitors have the disadvantage that significant quantities of Thermodynamic Hydrate Inhibitor material may be required to prevent hydrate formation, for example; typically 10 to 40-vol. % of methanol may be required to be added to the produced water of a system. There may also be safety issues that will need to be considered when considering the storage, transportation and handling of such large quantities of substances such as methanol.

The effective required Thermodynamic Hydrate Inhibitor dosage depends on the driving force for hydrate formation experienced in the system which is represented by the quantity ‘subcooling’. Subcooling is defined as the difference between the hydrate dissociation temperature and the system operating temperature at a given pressure. The higher the subcooling, the more severe the system conditions and the greater the driving force for hydrate formation. The effective dosage of a Thermodynamic Hydrate Inhibitor required to be used in the system increases as the subcooling increases. Obviously, this may lead to significant operational expenditure (OPEX) costs and logistical challenges when operating offshore systems, especially as the subcooling experienced in a system increases.

Partly due to the disadvantages of Thermodynamic Hydrate Inhibitors, the development of Low Dosage Hydrate Inhibitors (LDHI) has occurred over the last 15-years. LDHIs are so called as they can be successfully applied at lower dosages when compared to Thermodynamic Hydrate Inhibitors. LDHIs differ from Thermodynamic Hydrate Inhibitors in that LDHIs do not shift the thermodynamic equilibrium of hydrate formation but rather they become involved in the mechanism of hydrate formation in such a way as to interfere and modify the formation of hydrate crystals. These LDHIs are classified depending on the way in which they modify the hydrate crystal formation mechanism. The main two categories of LDHI are the Kinetic Hydrate Inhibitors (KHI) and the Anti-Agglomerants (AA). However, there are other surfactants which act as hydrate inhibitors by dispersing hydrate crystals as they form [10].

KHIs are typically water soluble polymers which interfere with and delay hydrate crystal nucleation and the initial crystal growth process [11]. They act in an analogous way to scale inhibitors in that they inhibit the formation of small crystals by their interaction with crystal growth sites. Clues to the chemical structures suitable for use as KHIs came from the observation in nature that certain fish had the ability not to freeze in sub-zero seawater temperatures. This was found to be due the ability of the fish to produce a protein that (like a KHI with a hydrate crystal) attached to an ice crystal and inhibited the further growth of the ice crystal [12]. The effect of the KHI is to slow down the kinetics of hydrate crystal formation and increase the induction time for hydrate formation. First generation KHIs were based on polymers of pyrrolidone or caprolactam ring based structures [13]. However these first generation KHIs also had limitations, such as the subcooling limits and the time limits to their effectiveness. The first generation KHIs were effective at controlling hydrates at up to 8°C subcooling for up to 24-hours. Kelland et. al. noted this when he proposed that the first generation KHIs had upper limitations on the subcooling that they could effectively control (of 10°C) [14].

If the severity of the system exceeds the effectiveness of the KHI then a rapid formation of hydrate material can occur. KHIs effectively provide a certain amount of hydrate inhibition time during which it is intended that the produced fluids are moved through and out of the hydrate forming conditions of the production process (by the operator). Ideally, the KHI treatment is designed such that the KHI induction time is greater than the produced fluids' residence time in the hydrate region. The risk of the hydrate inhibition time being exceeded needs to be evaluated as part of the hydrate management strategy and adequate contingency plans put in place (such as possible system depressurization).Subsequent development of second generation KHIs and even third generation KHIs has extended the limit of subcooling effectiveness up to 11 to 13°C (for days to weeks depending on the subcooling).

KHIs have the advantage of requiring lower dosages than Thermodynamic Hydrate Inhibitors and the associated OPEX savings this brings about. KHIs also reduce the risk due to storage and transportation of large quantities of Thermodynamic Hydrate Inhibitor. KHIs also are not limited by the water cut experienced in the produced fluids or by gas to oil ratios and generally, KHIs are relatively environmentally friendly.

There are, however, many offshore systems that operate under higher subcoolings that can't be optimally controlled using KHIs alone. In systems with higher pressures and cooler temperatures, subcoolings of higher than 10°C are common. In deepwater systems, subcoolings of the order of 20°C are not uncommon and even higher subcoolings in ultra-deepwater systems can occur [15]. This led to the development of Anti-Agglomerant (AA) hydrate inhibitors [16].

Anti-Agglomerants allow the hydrate crystals to form but in doing so, the hydrate crystals are kept small and non-adherent. These sub-micrometer sized hydrate crystals are well dispersed in liquid hydrocarbon, thus allowing the hydrates to be transported in the production fluids, as fluid viscosity remains low. The AA molecule functions via two chemical groups within its structure that have two important functions. Firstly, part of the AA is incorporated into the hydrate crystal structure [6]. This is typically an organic quaternary ammonium or phosphonium salt. Secondly, the AA has a long hydrocarbon 'tail' that makes the combined 'hydrate crystal – AA' structure soluble in hydrocarbon fluids preventing the formation of larger hydrate crystals.

Due to their mechanism of hydrate inhibition, AAs require the presence of a liquid hydrocarbon phase (condensate or oil), typically with a water cut of < 50 to 75 % and a Gas to Oil ratio (GOR) of < 100,000 scf/stb. AAs have the significant advantage that they are not restricted by the subcooling of the system (seen to be effective at subcoolings above 22°C). They also perform well regardless of the system's residence time in the hydrate region, including extended shut-ins of > 2-weeks. This makes the AA application rate the most cost effective at higher subcoolings.

COMBINATION PRODUCTS

In an effort to further lower the costs of offshore production for operating companies, developments and advances have been made in the formulation, testing and application of combination products. Instead of having a separate chemical application of LDHI or corrosion Inhibitor (CI) or even other inhibitors such as Paraffin Inhibitors (PI), it is possible to produce chemically compatible formulations of these inhibitor chemistries. These include LDHI/CI, LDHI/PI and even LDHI/CI/PI combinations. LDHI combinations with scale inhibitors or asphaltene inhibitors are also under development. Here we will focus on the development of effective combined KHI/CI products.

Offshore chemicals may be applied via umbilical lines where one umbilical line may be used, for example, for a CI and a separate umbilical line may be used for a KHI. Through the use of combination products, fewer umbilical lines would be required – as only one line would be needed for the KHI/CI application. The use of combination products may also lead to potentially less weight due to chemical storage overall, a smaller number of storage tanks and application pumps. This leads to CAPEX savings and reduced OPEX costs such as maintenance costs.

EXPERIENCE OF DEVELOPING COMBINED KHI/CI PRODUCTS

Opinions in the oil industry vary concerning the formulation of effective combined KHI/CI products. Some in the industry have come to the false conclusion that effective KHI/CI combination products can't be formulated. Our experience has shown that this is not the case. Through extensive work on a series of long-term projects Baker Petrolite has been able to develop effective KHI/CI products for a range of applications and these are illustrated below.

EXPERIMENTAL DETAILS

KHIs were evaluated using high pressure rocking cells and autoclaves.

KHI Rocking Cell Test Apparatus

Baker Petrolite's gas hydrate rocking cell test apparatus consists of individual pressurized rocking cells (see Figure 1). Each cell is equipped with a sight glass to enable visual observations to be made. Each cell can be used with field fluids at field pressures. In a typical experiment, each cell is charged with brine, oil (or condensate), and an inhibitor chemistry package. Once the liquids are in place, the cells are then pressurized to the target value with a suitable hydrocarbon gas mixture and placed in a temperature controlled bath.

Figure 1: High pressure hydrate rocking cells for KHI evaluation experiments

The cells are either rocked (to simulate flow conditions) or held static (to simulate a shut-in) during the course of each experiment. The rocking motion, when employed, causes added agitation.

The window in each cell allows visual interpretation of the fluid. Computer software monitors and records the pressure of each cell throughout the test. The monitoring of cell pressure is particularly useful for Kinetic Hydrate Inhibitors (KHI) as cell pressure decreases as hydrate formation occurs.

Synthetic gas compositions as close as possible to those expected in the field are used. Gas samples from the field are also used where possible.

KHI Autoclave Test Apparatus

Gas hydrate experiments were also carried out using high pressure autoclaves. Each thermally jacketed autoclave is equipped with a boroscope to enable visual observations to be made. Hydrate formation can also be detected by pressure monitoring. Hydrate formation leads to gas being incorporated into the hydrate solid structure and hence a drop in monitored pressure. A related increase in temperature due to the exothermic process of hydrate formation is also observed. The autoclave apparatus can be used with field fluids at field pressures. In a typical experiment, each autoclave is charged with brine, oil (or condensate), and an inhibitor chemistry package. Once the liquids are in place, the cells are then pressurized to the target value with a suitable hydrocarbon gas mixture and autoclave temperature is controlled using a constant temperature jacket with circulated coolant fluid. The fluids are agitated using a magnetic stirrer.

Visual observations may be recorded through the use of a video recorder system. A schematic of the apparatus is shown in Figure 2.

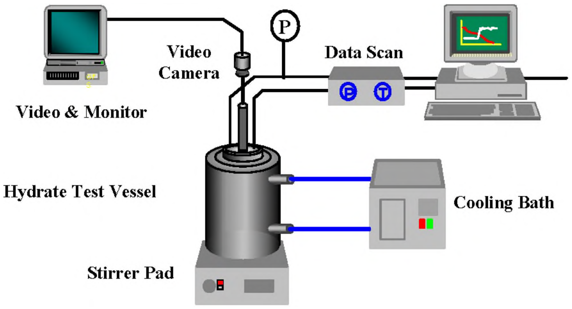

Figure 2: High pressure autoclave for KHI evaluation experiments

Corrosion Inhibitor Test Apparatus

Specifications for corrosion inhibition can be achieved using a range of specialized tests at Baker Petrolite. For example, Linear Polarized Resistance (LPR) tests can be used to monitor CI performance. A KHI/CI package can be monitored using this test (or other specialized tests as required) to measure corrosion inhibition performance.

The LPR test utilizes a sealed glass vessel containing test fluids. Access ports to the vessel allow an LPR (Linear Polarized Resistance) probe to be inserted and a gas sparge to be applied. The temperature of the vessel can be controlled throughout the test.

In this test, brine and an appropriate liquid hydrocarbon are allowed to deoxygenate using a continuous gas purge, which is maintained throughout the test. Continuous LPR monitoring is used during the test to measure the corrosion rate. Vessels can also remain uninhibited for the duration of the test to establish blank corrosion rates (for comparison to the KHI/CI combined inhibitor packages).

PRODUCTION SYSTEMS CONSIDERED AND KHI/CI PRODUCTS SUCCESSFULLY DEVELOPED

The following five systems are considered to show how a combined KHI/CI product (or KHI used in conjunction with a CI) was successfully developed in each case.

System A

A summary description of this system is given below in Table 1. Initially a KHI alone was developed for this system. However, due to the benefits of using a combined product, a KHI/CI product was subsequently developed.

KHI performance was tested using the rocking cells and autoclave equipment described above. It was noted that the candidate CIs tested for potential use with the KHI could have significant effects on the KHI efficacy. Certain CIs could significantly impact the efficacy of the KHI and its ability to inhibit hydrates. However, after an extensive development program, Baker Petrolite has been able to develop CIs which can be successfully incorporated into the KHI/CI package and still enable both the KHI and CI functions of the product to perform well.

Location	Offshore North Sea
System fluids	Gas / Condensate / Brine
Subcooling controlled	Approx. 10°C
KHI performance	No hydrates for > 48-hours
CI performance	< 1 mpy > 99 % protection
Product developed	KHI initially. Development led to a combined KHI/CI.

Table 1: Description of System A

This led to the successful application of the combined KHI/CI (described below in Case History #1).

System B
An outline summary of this system is given below in Table 2. A combined KHI/CI package was desirable from the outset of this project.

Location	Offshore North Sea
System fluids	Gas / Condensate / Fresh water
Subcooling controlled	Approx. 8°C
KHI performance	No hydrates for > 80-hours
CI performance	< 0.4 mpy > 99.9 % protection
Product developed	Combined KHI/CI

Table 2: System B description

Improvements during product development included the use of a more environmentally friendly corrosion inhibitor – whilst still retaining product performance.

System C
This development (summarized in Table 3) did not require a combination product but required that the KHI and CI be chemically and physically compatible when the products were mixed. There was also to be no drop in performance of each product, when the two products were mixed, as compared with the performance obtained using each product on its own.

Location	Offshore Middle East
System fluids	Gas / Condensate / Fresh water
Subcooling controlled	Approx. 8°C
KHI performance	No hydrates for > 220-hours during emergency shut-down
CI performance	< 0.01 mpy > 99.9 % protection
Product developed	Seasonal KHI and continuous CI.

Table 3: System C description

The use of a novel KHI gave impressive hydrate inhibition in the presence of an environmentally friendly CI. The KHI gave good results (in the presence of the CI) during long shut-in periods as well as long flowing periods and also for shut-in / restart scenarios.

System D

A combined KHI/CI was desirable for this application with the option of additional injection of thermodynamic hydrate inhibitor (THI) due to the high subcooling in the system (see Table 4).

Location	Offshore North Sea
System fluids	Gas / Condensate / Fresh water
Subcooling controlled	Approx. 14°C
KHI performance	No hydrates for > 72-hours
CI performance	< 3 mpy > 98.5 % protection
Product developed	Combined KHI/CI with additional THI.

Table 4: System D description

Three candidate combined KHI/CI products were developed specifically for this system. Due to the high subcooling in this application the use of the KHI/CI products was supplemented with the use of a Thermodynamic Hydrate Inhibitor (THI). It was observed that the use of the THI in the presence of certain KHI/CI candidate products could impact on the performance of the KHI. The choice of CI components was identified as a factor (which upon addition of the THI) was causing solubility changes in the system, causing the active KHI material to be withdrawn from the gas-liquid interface where it was needed most. This led to the optimization of the CI components. After further development a successful KHI/CI material was developed which could give the required KHI (and CI) performance in the presence of the additional THI. Further work indicated that the level of environmentally friendly CI could be increased (if required) in the combined KHI/CI product without compromising the KHI performance.

System E

This system required a combined KHI/CI. The formation of structure I hydrates was also occurring in this system. Structure I hydrates are less common than structure II hydrates. Hydrate structure I forms when the majority of the gases are smaller than propane. The majority of natural gas systems are hydrate structure II with gas compositions containing > 3-4 mole % molecules larger than ethane. The system is summarized in Table 5.

Location	Offshore North Sea
System fluids	Gas / Condensate / Fresh water
Subcooling controlled	Ranging between Approx. 6°C and 8°C (Hydrate structure I)
KHI performance	No hydrates for > 52-hours
CI performance	< 0.01 mpy
Product developed	Combined KHI/CI.

Table 5: System E description

Excellent CI results were obtained and the product developed for this system also used a novel KHI with further improved environmental characteristics.

COMMERCIAL APPLICATION

The KHI and KHI/CI products developed (as described above in system A) were successfully applied in the field as described below.

Case History #1

The use of a KHI was implemented by a major operator in an UK North Sea offshore application after the operator had experienced problems with the use of ethylene glycol as a Thermodynamic Hydrate Inhibitor. Production was principally gas and was being produced via a subsea template. The operator had been using the addition of ethylene glycol to inhibit the formation of hydrates in a 12” diameter, 16-km subsea gas flowline. Approximate daily production rates are given in Table 6 with production conditions provided in Table 7.

Gas / MMscfd	***Condensate / Bcpd***	***Water / Bwpd***
80	150	500 – 3000

Table 6: Approximate daily production rates for Case History #1

Flowing wellhead p / bar	***Shut-in wellhead p / bar***	***Flowing wellhead T / °C***	***Shut-in wellhead T / °C***
65	150	36	4

Table 7: Production conditions for
Case History #1

Due to increasing water production and rising salt levels (~80,000 ppm) the regeneration of ethylene glycol became problematic due to salt precipitating out in the heating bundles. This resulted in frequent shut-downs of the ethylene glycol regeneration system for cleaning and maintenance. It also led to the subsequent discharge of the contaminated ethylene glycol directly to the sea. Additionally, maintenance costs for this system were escalating due to increasing corrosion failures. Due to the negative environmental impact of discharging ethylene glycol, the increasing maintenance costs and the costs for replacement ethylene glycol, it was decided to investigate alternative hydrate inhibition technologies, i.e. KHIs. The most suitable LDHI was a KHI due to the high volumes of gas being produced and relatively low levels of water and condensate produced.

Prior to KHI implementation, an extensive laboratory testing program was carried out under field conditions using worst case shut-in conditions. The KHI selected for field trial showed good hydrate inhibitor performance at sub-coolings of 10°C. Laboratory testing showed the KHI provided a similar level of inhibition as ethylene glycol but only required between 10 – 15% equivalent chemical. Treatment costs using the KHI were 40% lower than when using ethylene glycol. The KHI selected showed low emulsion-forming tendency, had good material compatibility properties, had an excellent environmental classification and provided lower treatment costs.

The KHI was successfully applied in the field at the dosage indicated by laboratory tests. However, during the field trial stage, offshore performance monitoring established that salt levels were higher than first thought and approaching 250,000 ppm when specific wells were producing. This significantly reduced the sub-cooling experienced in the system and subsequently the amount of KHI required and applied. Overall treatment saving costs were estimated at 80 % with additional operational savings being realized through reduced tank rental, logistical expense and maintenance costs. The use of the KHI enabled production targets to be maintained, which in turn meant that the required delivery volumes and schedules could be met.

Further product development was then carried out with a corrosion inhibitor (CI) being successfully formulated with the KHI to give a combined KHI/CI product. This led to further cost savings for the operator. The KHI and the combined KHI/CI equivalent were successfully applied in the field for 18-months before the requirement for hydrate inhibitor was no longer necessary due to the declining reservoir pressure – moving production out of the hydrate forming region. KHIs provided the benefit of having good environmental characteristics helping to minimize environmental impact and the KHI usage also helped to lower overall project costs – as illustrated in Table 8.

Application location	Offshore UK North Sea
LDHI applied	KHI initially. Development led to a combined KHI / CI.
Thermodynamic inhibitor replaced	MEG replaced by using 10 – 15 % equivalent KHI.
Treatment cost savings	80 %

Table 8: LDHI applied and benefits obtained for Case History #1

CONCLUSIONS

Corrosion Inhibitors can have a significant impact on the efficacy of Kinetic Hydrate Inhibitors (KHI). Baker Petrolite has considerable experience in developing effective combined KHI/CI products and this has been demonstrated over a range of systems. Initial work focused on the formulation of suitable effective KHI/CI combinations. This has now progressed to the use of more environmentally friendly component KHIs and CIs whilst maintaining combined product efficacy.

KHIs have been developed which work as combined KHI/CI products. KHIs have also been developed which can be used seasonally with continuous CIs whilst maintaining the effectiveness of both KHI and CI.

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