QUALIFICATION OF LOW DOSE HYDRATE INHIBITORS (LDHIS): FIELD CASES STUDIES DEMONSTRATE THE GOOD REPRODUCIBILITY OF THE RESULTS OBTAINED FROM FLOW LOOPS.

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ABSTRACT

Replacement of the traditional thermodynamic hydrate inhibitors (methanol and glycols) in multiphase applications is highly desirable for Health, Safety & Environment (HSE) considerations and for investment costs savings.

Low Dose Hydrate Inhibitors (LDHI) are good candidates to achieve this objective and their interest is growing in the E&P industry. There are two types of LDHI: the Kinetic Hydrate Inhibitors (KHI) and the Anti-Agglomerants (AA) also called dispersant additives.

The main challenge with LDHIs is that they require the unprocessed effluents to be produced inside the hydrate stability zone. It is then of the utmost importance to select, qualify and implement properly LDHIs, so that their field deployment is performed with success.

But due to the very stochastic nature of the nucleation step, the hydrate crystallisation process leads to very large discrepancies between performances results carried out at lab or pilot scales.

In order to overcome this difficulty, we have developed an in-house special protocol which is implemented prior to each qualification tests series. This in-house 15 years old protocol consists in conducting each tests series with a fluids system having previously formed hydrates in a first step but followed by a dissociation step at moderate temperature for a few hours.

This paper presents results selected from several field cases studies and obtained from our 80 bara and 165 bara flow loops. They show the very good reproducibility obtained with and without LDHIs.

In the case of KHI, where the stochastic nature of the nucleation step is very critical, the results show that the deviation on the "hold time" for a given subcooling is less than 15%.

Keywords: gas hydrates, kinetic hydrate inhibitors, hydrate flow loop, hydrate test results reproducibility

NOMENCLATURE

LDHI Low Dose Hydrate Inhibitor KHI Kinetic Hydrate Inhibitor AA Anti-Agglomerants MEG Mono Ethylene Glycol CAPEX Capital Expenditure OPEX Operating Expenditure FPU Floating Production Unit FPSO Floating Production Storage and Offloading SCFD Standard Cubic Feet per Day WHFP Well Head Flowing Pressure ^{*} Corresponding author: Phone: +33 559 83 67 13 Fax +33 559 83 42 99 E-mail: philippe.glenat@total.com

INTRODUCTION

From a flow assurance point of view, gas hydrate formation is undoubtedly dreaded as the major risk of plugging the oil and gas production systems. This is why a lot of studies are generally performed in the Project Development phase to compare several solutions, to select the one which is the best compromise between cost and associated risks, and to finally develop a proper hydrate control strategy that will have to be implemented on the field.

Hydrates control by keeping the production system outside the hydrate stability zone

The crystallisation and agglomeration of hydrate particles generally lead to solid plugs which can block the production systems (tubing, wellhead, jumpers, manifolds, pipelines, valves), and thus result in the shutdown of production facilities. Hydrate plugs can be the result of deposits growth and/or of hydrate crystals agglomeration. The removal of hydrate plugs is generally difficult to achieve. A shutdown of several days may be necessary prior to the restarting of the production and, indeed, pipeline abandonment may occur. This is why, up to some years ago, all of the oil and gas fields were developed with the objective of keeping the effluents outside the hydrate zone, both in flowing and transient (shut-in/restart) conditions.

There are two usual ways of maintaining the pressure and temperature conditions outside the hydrate formation region.

This can be achieved by shifting the hydrate stability zone towards lower temperatures by means of the injection of thermodynamic inhibitors such as methanol or MEG (Mono Ethylene Glycol). This can also be accomplished by insulating, or even heating, the production systems to reduce heat losses between the hot produced fluids and the cold environment (sea bed for instance). These two methods are used for decades and are fully field proven. However, both solutions have significant economical impacts and/or technical limitations when applied to offshore production fields.

Regarding the thermodynamic inhibitors, they are effective at rather high concentrations in water (30 to 60 wt%), resulting in potentially high concerns about Health, Safety and Environment (HSE) risks. Methanol injection leads to a high operational expenditure (OPEX) level and also needs large size storage facilities. As for MEG injection, it needs installation of reboilers for glycol regeneration as well as storage requirements. Both MEG and methanol account for typical losses [1] [2]. Moreover, the refineries tend now to limit the methanol concentration allowed in the oil and condensate which can cause serious problems in desalting operation and water management. Similarly, severe penalties are now applied on the gas and on the oil containing too much methanol.

Regarding the insulation, in addition to its high capital expenditure (CAPEX) level and the technical challenge faced by the design and installation of high performance insulation, it will not prevent entering the hydrate formation region during a long enough shutdown. Consequently, additional methods have to be anticipated for shutdown/restart procedures. Nevertheless, a well designed insulation generally prevents hydrate formation during normal operation conditions and simultaneously avoids potential wax deposition.

For all these reasons, there is today a strong economical incentive to replace methanol, MEG or insulation every time and everywhere it is possible.

New means of hydrate control with the production system inside the hydrate stability zone

New types of chemicals, called Low Dose Hydrate Inhibitors (LDHI), have been considered as the most interesting option regarding the replacement of methanol, MEG or insulation.

But, because of their low dosage, LDHI do not shift the hydrate stability zone at all, contrary to the thermodynamic inhibitors; so that the unprocessed effluents are allowed to transit inside the hydrate stability zone. This is the resulting main challenge from a flow assurance point of view when using LDHIs in oil and gas production systems. As a consequence, the use of LDHI is not as straightforward as that of the thermodynamic inhibitors: based on an associated risk analysis, a proper hydrate management strategy has to be developed for the field in order to define adequate contingency procedures and back-up solutions, the of including possibility complete depressurisation of the production system, preferably from both ends.

There are in fact two types of LDHI: the Kinetic Hydrate Inhibitors (KHI) and the Anti-Agglomerants (AA) also called dispersant additives. The development of LDHIs has been subjected to a lot of research works for the last eighteen years, and to several field testing and deployment for the last twelve years ([3] to [17]). For one or two years, a growing interested has been noted for the LDHI technologies even if they are not yet extensively used.

LDHIs are so called as they can be efficiently used at dosages far lower than that of the thermodynamic inhibitors: the required concentration for these additives is currently expected in the range of 0.5-3 wt% in water. But, in order to avoid any confusion, it is worth mentioning that these dose rates are low compared to methanol or MEG ones, but they remain rather high when compared to the dosages of other field chemicals such as scale, wax or asphaltenes inhibitors.

Owing to their low dosage, the most interesting economic advantage expected from LDHIs should have been the reduction of OPEX. But it is not the case because their price is still very high (4 to 5 Euros/l), so that their dose rate multiplied by their price leads to about the same OPEX cost as for methanol!

This is why on most of the oil fields, where the water flow rate becomes unavoidably very high at a certain field life time, it is economically redhibitory, just as it is for methanol or MEG, to contemplate a continuous injection of LDHIs.

In fact, the main economic incentive of using LDHIs is today the large reduction of CAPEX via the reduction of the size of the storage, pumping and piping facilities; they also have the benefit that they are far less volatile and flammable, and relatively more environmentally friendly than methanol, resulting in the reduction of HSE risks.

Kinetic Hydrate Inhibitors. A KHI is a chemical product composed of active matters formulated in a solvent. The active matters are at least partially water soluble polymers with eventually synergist products, and the solvent is composed of MEG and/or heavy alcohols. They act by delaying hydrate nucleation step and by slowing down the initial crystal growth during a finite period commonly defined as "hold-time". The hold-time due to KHI is dependent on the sub-cooling but also on the test pressure [18]. As a consequence, the efficiency and thus the applicability of a KHI depend upon two factors: first of all the subcooling to which the produced effluents are exposed, and then the residence time of the water inside the hydrate stability zone.

For a given pressure, the subcooling can be defined as the difference between the thermodynamic hydrate forming temperature (also called dissociation temperature) and the ambient temperature (seabed temperature for instance). The subcooling is indeed the "driving force" of the kinetics of hydrate crystallisation; so, the higher the subcooling, the lower the efficiency of the KHI. There is in fact an absolute subcooling limit above which the hydrate formation is guite instantaneous, whatever the dose rate of the KHI. Today, this limit can be estimated at around 14-15°C for the best KHIs.

Then, for a given subcooling, the applicability of a KHI depends on its ability to delay hydrate formation for a time longer than the residence time of the water inside the hydrate zone.

As a consequence, the use of KHIs, on a continuous injection basis, is limited to situations where the subcooling is rather mild (technical limitation) and where the water flow rate is rather low (OPEX limitation).

That is why KHIs have been originally successfully applied on some small fields exhibiting mild conditions in the UK sector of the North Sea and in the US onshore.

Regarding TOTAL Group experience with KHI, two field tests were carried out in France in 1997 [19], and in Argentina in 1999 (not published). But our first actual field experience with KHI is that of South-Pars 2&3 in Iran [20]. It was probably the first one of this size (2 x 1000 MMSCFD) in the Middle East region. Field data have shown that the hydrate risk is lower than the one initially expected due to too low sea bottom temperatures used in the basis design. But since then some field upsets have clearly demonstrated that the hydrate risk is definitely real for South-Pars 2&3. The success of this first application was a strong incentive to use a KHI as the base case for hydrate prevention on Dolphin, a large gas field situated offshore Qatar delivering 2 x 1300 MMSCFD. The KHI injection has been started in November 2007 to protect the sealines and the onshore slug catcher.

Anti-Agglomerants. AAs are generally surface active products mixed in a solvent. They can be water or oil soluble depending on the technology used. Contrary to KHIs, they do not avoid hydrate formation but they mitigate their growth and agglomeration, so that the tiny hydrate crystals can be transported in the oil phase as a kind of slurry. And, contrary to KHIs also, they can sustain high subcooling levels, up to 18-20°C.

So in the cases where waxes are not an issue, the potential use of AAs could allow to get rid of the insulation, or at least to reduce it, resulting in significant CAPEX savings. But their main drawback is that their efficiency is limited to a certain watercut: as soon as the watercut is higher than 30-40%, the hydrate particles concentration in the slurry becomes so high that AAs are no longer able to allow the transport of the suspension.

As a consequence, the potential use of AAs, on a continuous injection basis, is limited to situations where the watercut is rather low (technical limitation) and where the water flow rate is rather low (OPEX limitation).

Because of their OPEX limitation, AAs are mainly used today in transient situations on oil fields, especially to allow reducing the methanol injection and thus to quicken the cold restart of wells up to a certain watercut.

In the future, the continuous injection of AAs will be possible to contemplate most probably when the wellhead (or downhole) water separation has become a field proven technique.

HYDRATE LOOPS TESTING FACILITIES

Contrary to methanol or MEG which are "universal" inhibitors, a LDHI has to be tailored to each given situation. This is because its formulation has to be adapted to the physicochemistry of the fluids system, i.e. the composition of the gas phase (which can lead to hydrates of structure I or II), the nature of the oil (acidic, asphaltenic), the water (condensed water or brine) and the presence of the other production chemistry additives (especially corrosion inhibitors). Furthermore, the impact of the presence of the LDHI on the downstream process (oil/water treatment and separation. water disposal, condensate stabilisation, gas treatments) has also to be taken into account. This is why, before their eventual deployment on a field, the LDHIs have to be carefully selected via qualification tests carried out in experimental set-ups allowing to simulate operating conditions as close as possible to the field ones.

To be able to evaluate the efficiency of the LDHIs in-house, a first hydrate flow loop was built in 1990 with a service pressure of 80 bara. But, with the development of deep offshore fields, this pressure was less and less representative of the actual field pressure. So a new hydrate flow loop with a service pressure of 165 bara was built in 2005 and started early 2006. These two bench scale pilots differ by the service pressure, but have the same shapes and features, the same control devices and the same data acquisition system. Hereafter is a description of the high pressure hydrate loop. A simplified scheme and a photograph of the new hydrate loop facility are shown in figures 1 and 2.



Figure 1: Simplified flow scheme of the 165 bar hydrate loop



Figure 2: Photograph of the 165 bar hydrate loop

Description of the 165 bara hydrate loop facility The hydrate loop facility is based on the principle of a gas saturated liquid circulating loop. It can be operated night and day. This bench-scale unit is mainly composed of a pipe, a pump and a storage tank. Except the stator of the pump which is made of a carbon charged rubber, all the other parts of the unit in contact with the process fluids are made of 316L stainless steel. Any type of gas (except H2S because of the stator material), any type of oil or condensate, any type of brine can be used. The pipe has an inner diameter of 1 inch and a total length of 35.6 m, resulting in a liquid hold-up of 18 litres. The shape of the loop is a double vertical ring of 32 m linked to the inlet/outlet of the pump. The whole pipe is jacketed in order to control its temperature via the circulation of a cooling/ heating fluid inside the jacket. The Moineau type pump is from PCM. It is designed to circulate fluids at a pressure as high as 165 bara and a temperature ranging from 50 to 0 °C. The maximum pressure drop available between the inlet and the outlet of the pump is 20 bar. The pump is equipped with a speed change device and it can provide flow rates up to 6 m^3/h resulting in liquid velocities up to 3 m/s. The pump is also equipped with a jacket in order to circulate the cooling/heating fluid and thus control its temperature, both in flowing and shut-down conditions. The main advantage of this type of pump is its low shearing power: it is able to circulate a slurry with particles of 1cm in diameter without crushing them. Its main drawback is the large volume (26.5 liters) located between its motor/gears and the rotor/stator body where the fluids velocity drops and where, as a consequence, weak emulsions may separate or weak suspensions may deposit more easily. But, on the other hand, in a real pipeline, there are possible low points where the liquid fraction may be stagnant for a while; consequently, this pump volume may possibly be rather representative, at a smaller scale, of such a low point. A storage tank of 90 liters is used to fill the loop with a given load composition, and allows to add some of the ingredients (water or oil or additives) to the load without having to drain and clean the loop after each single test. An auxiliary high pressure pump is used to add the ingredients without having to depressurize the unit, or to stop the fluid circulation. Finally, the loop is also equipped with

- a mass flow meter able to deliver the density of the process fluid in addition to its mass flow rate. The density is provided even during a shut-down because its measurement is independent on the flow rate measurement. It is located in a rather low part of the loop, 2 m after the pump outlet.

- two dp cells (0-20 bar) able to measure the pressure drop between the inlet/outlet of the pump and between the inlet/outlet of the 2 vertical rings of the pipe.

- a compressor from Burton-Corblin: it is designed to compress the gas up to 200 bar, and it is used to deliver the gas to the unit at the desired pressure.

- a gas make-up system controlled by a pressure regulator: the purpose of this device is to keep constant the desired pressure all over a test, even when the temperature decreases and even when hydrates form. The gas make-up added to the unit is measured by 2 gas meters (with 2 different ranges) placed upstream the pressure regulator. The measurement of this gas make-up flow rate is then used to calculate the theoretical amount of water converted into hydrates during a given test.

- various temperature probes able to measure the temperature at different points of the unit, especially at the inlet/outlet of the process fluids (inlet/outlet of the loop) and at the inlet/outlet of the cooling fluid.

- a cooling/heating apparatus, able to provide a cooling or heating speed ranging from 1 to 25° C/h and to maintain the whole unit (pipe + pump + storage tank) at temperatures ranging from -10 to + 60°C. Ethanol is circulated by the apparatus in a heat exchanger where the cooling/heating fluid (a blend of water and ethanol) is cooled or heated at the desired value. Thanks to this exchanger, when the test temperature is reached, the temperature gap between the inlet and the outlet of the process fluid is normally less than 0.2°C, and it is the same for the temperature gap between the inlet and the cooling fluid. Furthermore, the temperature gap between the process fluid and the cooling fluid is less than 2°C.

- a computerized system is devoted to data acquisition in real time and modification of the set points; safety is ensured by a series of electronic regulators, one per every control loop.

HYDRATE FORMATION ONSET REPRODUCIBILITY

Generally speaking, the reproducibility of the hydrate formation onset in a lab scale experimental set-up is rather poor: this is a general rule that applies whatever the experimental set-up (lab cell (autoclave or rocking-cell types), mini or pilot flow loop) and whatever the system (with or without the presence of LDHI). The poor reproducibility of hydrate formation onset is due to the stochastic nature of the nucleation step of the hydrate crystallisation [21], and it is particularly exacerbated in the case of lab cell tests [22]. Incidentally, there are very few publications that give clearly and honestly the actual spread of the tests results!

The poor reproducibility of hydrate formation onset is of course detrimental to the proper interpretation of any type of hydrate test, but it is absolutely critical for KHI efficiency evaluation because it results in a very large spread of the hold times; and, on top of that, very often, it even does not allow to clearly distinguish between the blank and the KHI tests results!

To overcome this stochastic nature of the nucleation step of hydrate crystallisation, we have developed an in-house special protocol which is performed prior to each tests series with LDHIs.

Development of a test protocol to improve the hydrate formation onset reproducibility

When we started running our 80 bara hydrate flow loop, 15 years ago, we were sometimes faced to the difficulty of forming hydrates despite the fact that the uninhibited system was inside the hydrate zone at subcoolings as high as 10°C. From time to time, it was even necessary to decrease the temperature slightly below zero (-1°C/-2°C) in order to force forming ice crystals that acted as seeds for starting the hydrate formation onset; this method was very efficient to force forming hydrates, but was not at all satisfactory to evaluate the performance of inhibitors like LDHIs. After this first hydrate formation, the system was warmed up to a temperature outside the hydrate zone in order to dissociate the hydrates. We observed that if the warming temperature was not too high, i.e. not too far from the thermodynamic hydrate temperature, it was then far easier and quicker to form again hydrates with a system that had already formed hydrates, and, on top of that, we observed that the hydrate formation onset was then far more reproducible from test to test.

The basic phenomenon behind this might be that the hydrate clusters remaining in the system after the first hydrate formation act as the heterogeneous germs that are present in real systems and that avoid, or at least reduce, the stochastic behaviour of the nucleation step.

Based on this idea, we have developed a very simple protocol, as illustrated in figure 3. This protocol has been implemented for 15 years on our flow loops, and it has proved to be very efficient to overcome the stochastic nature of the nucleation step of hydrate crystallisation.

The phenomenon on which our protocol is based upon is sometimes called "hydrate water memory" and has been more recently investigated by research organisations [23 to 26] and is even foreseen to be used to identify hydrate history of real produced waters [27].



Figure 3: Protocol developed to improve hydrate test reproducibility in TOTAL flow loops.

 T_{hyd} is defined as the hydrate dissociation thermodynamic temperature, below which the system enters the hydrate stability zone at a given pressure. The protocol consists of the following successive steps:

- the temperature is decreased at a rate of 10° C/h until hydrate formation onset,
- the system is warmed up to a temperature only 10° C above T_{hyd} during 2h in order to dissociate hydrates but also in order to leave some hydrate clusters present in the system.

At this point, the actual test is started. At the end of the test, the temperature is again increased up to 10° C above T_{hyd} in order to repeat the same protocol, so that the system is ready for another test.

This protocol has been successfully applied since then to all the flow loop tests series we have carried out so far [18] whatever the system, inhibited or not. As a consequence, no attempt has ever been made to try to "optimise" it.

But quite recently, the test protocol we had developed for our loop tests has been applied to screen KHIs into lab cell (autoclave type) experiments [28]. It took some time to adapt the protocol to the specificity of the cells, but it ended up with an outstanding improvement of the reproducibility of the tests results, and above all, it proved to allow a clear discrimination between the blank and the KHIs tests results.

CASES STUDIES

Hereafter are 4 examples of studies carried out within the frame of technical assistance to Field Developments. They illustrate the good reproducibility of the flow loop tests results obtained thanks to the above described protocol.

Case study n°1:

It is an oil field located 80 km offshore in the Gulf of Guinea, in water depths ranging from 600 to 900 m. The initial Phase 1 development plan for the Project comprises 12 subsea wells tied back to a FPU whose output, around 90,000 barrels per day at peak, will be exported to the onshore terminal. The field is scheduled to come on stream in 2008.

The fluids composition is such that hydrates of structure II may form. In normal steady state operation, the unprocessed fluids are well outside the hydrate region, thanks to the thermal insulation of the wellheads and pipelines. But during a production shut-down, the thermal insulation is designed to provide a cool-down time of 6 hours before the wellheads reach a temperature below which hydrates may form. So in case the shut-in lasts more than 4 hours, then the well preservation procedure will be started.

But, calculations had shown that, in one more exposed area, there are wells for which the cooldown time is limited to 3 hours, and for which the temperature will go 5° C below the hydrate avoidance temperature after 6 hours.

The continuous injection of a KHI has been contemplated for the wells of this particular area in order to delay possible hydrate formation for 3 hours with a maximum subcooling of 5° C at 90 bara, during a shut-in.

In this case, the purpose of the use of a KHI on these wells is thus to improve the available cooldown time in order to get the 6 hours required for the complete well preservation procedure, as for all the other wells. Four KHIs provided by 4 different suppliers were evaluated. Prior to each of the 4 test series, a blank test was systematically carried out with the uninhibited load (no KHI) to determine the hydrate formation delay at 5°C of subcooling and 90 bara. The blank test was in fact repeated two times with the first load before evaluating the first KHI, and then 3 times with each different load before evaluating each of the 3 other KHIs.

Table 1 shows that the resulting hold times were outstandingly reproducible.

subcooling = 5° C - P = 90 bara				
no KHI				
load n°	hold time (mn)			
1	55 / 60			
2	60			
3	60			
4	60			

Table 1: repeatability of blank tests (no KHI)

The hold time of a blank test being one hour, the hold time target for the KHI was set at 4 hours. This was achieved by adding 1500 ppm of a KHI in water. The test was then repeated, and table 2 shows both results that were obtained.

subcooling = 5°C - P = 90 bara KHI = 1500 ppm / water			
load n°	hold time		
1	4h05 / 4h55		
T 1 1 0 1 11			

Table 2: repeatability of tests with KHI (short hold time)

In this case, the repeatability is still fairly acceptable even if it is not as good as it is with the blank tests. Indeed, it seems it is a general trend when very short hold times are aimed at, especially with small KHI doses. Nevertheless, the deviation expressed as the difference (50 min) divided by the average (270 min) is less than 20%.

Case study n°2:

It is a sour gas/condensate field located offshore in the Persian Gulf about 70 km from shore in 55 m water depth. Two 36 inches production sealines route the untreated fluids to the on shore treatment plant. The maximum operating temperature and pressure are 90°C and 125 bar, respectively. The flow rate for each sealine is between 0.6 and 1.3 BSCFD for gas, 400 m³/h for condensate, and 10 m³/h for water at beginning of the field life.

The fluids composition is such that hydrates of structure II may form. A KHI mode was preferred to a MEG mode in order to cut the CAPEX costs. The target for the KHI was to delay hydrate formation for more than 8 days at 7°C of subcooling.

A lot of tests series were carried out both with the medium and the high pressure loops in order to evaluate various KHIs. But we did not repeat every test; first of all because the hold time target was rather long, and also because we are now pretty confident in the reproducibility of our results. Nevertheless, from time to time, we have repeated some tests in order to check that the repeatability was always good.

As an example, figure 4 illustrates the reproducibility of some tests results: with the KHI provided by the supplier A, two tests were carried out at 8° C of subcooling, and the resulting hold times showed a deviation of only 7% (308h and 330h respectively), whereas with the KHI provided by the supplier B, the hold times of the two tests carried out at 7°C of subcooling showed a deviation of only 6% (193h and 205h respectively).



Figure 4: repeatability of tests with KHI (long hold time).

Generally speaking, in this peculiar study, we have observed that, for a given subcooling, the deviation on the hold time is in any case less than 15%.

Case study n°3: it is a subsea lean gas/condensate field in the North Sea, tied back to an existing host platform via a single uninsulated 12 inches sealine. The nominal gas production is $6 \ge 10^6 \text{ Nm}^3/\text{d}$. The maximum WHFP is 130 bara and the WHFT is 35°C. From a flow assurance point of view, one critical issue is the prevention of hydrates in the 12 inches sealine. The rather low WHFT prevents the effective use of insulation. The current operating philosophy involves using a thermodynamic inhibitor for an initial production phase when only condensed water is produced. Following formation water breakthrough, the dose rate required for a thermodynamic inhibitor will make it logistically impossible to use on a disposable basis. There are also environmental concerns of dumping large volumes of these chemicals into the sea. An alternative solution therefore had to be found and the possibilities were either a thermodynamic inhibitor with a regeneration unit, or a KHI. Using

the KHI technology was assumed to be less expensive than building and operating a regeneration unit on the host platform.

But the application of the KHI technology was a real challenge which was twofold:

- the gas is essentially methane, which means that hydrates of structure I will form; and the formation of sI hydrates is problematic for inhibition with present KHIs because, up to now, most of these chemicals have been developed for structure II hydrates,

- the maximum expected subcooling is high (11°C), and, in addition, hydrate formation must be delayed for a relatively long time: a minimum of 120 hours (5 days) under flowing conditions.

In fact, it was impossible to find a KHI able to comply alone with this performance target. The solution finally studied was based on a combined MEG + KHI mixture: the role of the MEG is to shift the hydrate zone by 3° C, resulting in a subcooling of only 8° C (instead of 11° C) to be matched by the KHI. So the new performance target for the KHI was to delay hydrate formation for 120 h at 8° C of subcooling.

In fact, two tests series were carried out respectively in April and September 2006, with a different load and a different KHI sample. Obviously, the September results displayed on table 3 confirm a very good repeatability with those obtained five months before.

P = 130 bara, field condensate, brine = 37.5 NaCl g/l, watercut = 50%, liquid velocity = 1.5 m/s, cooling rate = 10°C/h, before MEG addition : Teq-hydrate = 13.5°C and subcooling = 11°C target = hold time > 120 h (5 days)						
test temperature (C°)	KHI (wt% in water)	MEG (vol% in water)	subcooling after MEG addition (°C)	April 2006 tests results	September 2006 tests results	
2.5	2	10	8,15	Fail at 0 h	Fail at 0 h	
2.5	3	10	8,15	Fail at 16 h		
2.5	4	10	8,15	Fail at 17 h	Fail at 20 h	
2.5	4	15	6,37	Fail at 72 h		
2.5	4	20	4,36	Pass > 160 h	Pass > 165 h	

Table 3: repeatability of tests with KHIs + MEG

Case study n°4:

It is an oil field located 135 km offshore in the Gulf of Guinea, in water depths ranging from 1200 to 1500 m. It is one of the world's biggest Projects started in 2006.

The production of the 37 wells is routed to a FPSO (Floating Production Storage and Offloading) whose treatment capacity is 240,000 bpd, and whose storage capacity is 2 millions bpd.

The fluids composition is such that hydrates of structure II may form.

In normal steady state operation, the unprocessed fluids are well outside the hydrate region, thanks to the thermal insulation of the wellheads and pipelines. For shutdown and restart situations, the Project has based the hydrate prevention strategy on conventional treatment with methanol.

But the Project has also considered that antiagglomerants could potentially be used for cold restart of wells, in order to avoid the injection of large quantities of methanol which is, besides, a source of pollution. This is indeed becoming now a more and more current practise.

The use of anti-agglomerant could at least be applicable for the early life of the field when the watercut is still limited to 30-40%. So we were asked by the Project to evaluate the use of AAs to facilitate quicker cold restarts of wells.

Some of the tests were repeated to confirm the "pass" result that was obtained. This was the case for the test carried out with 1 wt% AA from at 30% watercut.

As shown on figures 5 and 6, the hydrate formation onset was found to occur respectively 2h34 and 2h27 after the start of the test.



Figure 5 : test with AA.



Figure 6 : test repeated with the same AA Apart from the very good repeatability of the hydrate formation onset, the variations of all the

main parameters (pressure, temperature, pressure drop, flow rate, water conversion to hydrates) were found to exhibit a very similar behaviour in each test.

DISCUSSION AND CONCLUSION

Due to the stochastic nature of the its nucleation step, the hydrate crystallisation process leads to very large discrepancies between the results of performance tests carried out at lab or pilot scale, especially regarding the hydrate formation onset.

In order to overcome this difficulty, we have developed a special protocol which is implemented prior to each tests series. This protocol consists in conducting each tests series with a fluids system having previously formed hydrates in a first step, followed by a dissociation step at moderate temperature for a few hours.

Through the different case studies above described, we have demonstrated that the protocol provides an outstanding improvement of the reproducibility of the hydrate loop tests results. It has also proved to be reliable and robust in all situations, with and without LDHIs.

Furthermore, regarding the specific KHI efficiency evaluation, the protocol allows an unambiguous discrimination between the blank and the KHI tests results, which is absolutely essential for the performance appraisal of the KHI, and for getting the best chances of a successful field deployment.

Finally, why this protocol can provide a far better repeatability of the results and a very good discrimination between blanks and KHI tests?

The question is open of course, and we would be happy that high level researchers find the actual scientific reason.

In the meantime, our feeling is the following: in real oil & gas systems, the hydrate formation onset is very well repeatable because hydrate nucleation is mainly triggered by heterogeneous germination.

On the contrary, in a clean lab set-up, with fresh ingredients, i.e. in the absence of any hydrate precursors, the nucleation step is exclusively governed by the homogeneous germination that is well known to be completely stochastic.

So we believe that the controlled presence of hydrate precursors is a good way both to overcome the stochastic nature of the homogeneous germination, and to mimic the heterogeneous germination that governs the hydrate formation onset in real systems.

We have further evidenced [28] that the controlled presence of hydrate precursors in the testing

conditions results in significant shorter hold-times for KHI than when they are absent (homogeneous nucleation). Test procedures which do not allow mimicking such heterogeneous hydrate formation can then be considered as giving optimistic holdtimes of KHIs.

So we believe that the testing procedure described in the present paper also allows getting more realistic hold times of KHIs, which can then be up scaled to the oil and gas fields.

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