

"Experimental testing and evaluation of a kinetic gas hydrate inhibitor in different fluid systems"

Olav Urdahl¹, Are Lund², Lars Henrik Gjertsen¹ and Torstein Austvik¹

1 Statoil Research Centre, Field Development Technology, Posttuttak, 7005 Trondheim, NORWAY

2 SINTEF, Applied Chemistry, 7000 Trondheim, NORWAY

*Corresponding author

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Introduction

The development of offshore mature basins such as the North Sea is increasingly characterized by marginal reservoirs. Feasible economic development of these reservoirs requires a shift towards total subsea production systems without fixed or floating production platforms. Unprocessed or minimum processed reservoir fluids will be transported to a central processing facility or ultimately to shore. One of the key issues of total subsea production systems is multiphase flow technology with particular emphasis on gas hydrate control technology.

Subsea transportation of unprocessed or minimum processed well fluids over long distances today requires the use of large amounts of methanol or glycols for hydrate inhibition. The effect of these additives is to decrease the water activity to an extent that markedly reduces its ability to participate in hydrate formation, and thereby in a lowering of the hydrate formation temperature. The amount of inhibitor necessary to obtain the desired lowering of the hydrate formation temperature is substantial, usually in the range of 20-40 weight% of the aqueous phase. This has prompted the search for new types of additives capable of inhibiting hydrate formation at far lower concentrations (1-5).

Statoil performs intensive research on hydrates; methods to prevent hydrate problems as well as studies on the formation and removal of hydrate plugs. This paper focuses on the robustness of a commercially available additive from T. R. Oil Services (Hytreat 525) with respect to degree of subcooling, pressure, salinity of the aqueous phase and the impact from having a defoamer or a corrosion inhibitor in the system. The inhibitor is tested both at continuous flow conditions and at re-starts after shut-ins. Results from tests on two different condensate systems as well as two crude oils are summarized.

Experimental

The experiments were carried out in a high pressure loop formed as a wheel. The system is illustrated in Figure 1. The test wheel was filled with the desired fluid at a specified temperature and pressure, and then set under rotation. The rotation creates a relative velocity between the pipe wall and the fluid thus simulating transport through a pipeline.

The high pressure wheel is made from stainless steel with an inner tube diameter of 52.5 mm and a wheel diameter of 2.0 m. The volume is 13.4 liters. The wheel includes two high pressure windows for visual inspection, and one of these is equipped with a video camera.

The flow simulator is placed in a temperature controlled chamber. The temperature is controlled using a programmable regulator, a heating fan and a refrigeration system. The temperature development in the chamber as a function of time is preset in the regulator.

The wheel is attached to a motor/gearbox system enabling a variation of the peripheral velocity of the wheel between 0.3 m/s and 5.0 m/s. A torque sensor is installed as a part of the rotational shaft enabling torque measurements to be performed during rotation. Pressure and temperature sensors on the wheel have ranges of 0-250 bara and -10 to +150 °C respectively. All signals are transferred through cables and slip rings to a real time PC-based data acquisition system.

The accuracy of the measurements is estimated to be ± 0.2 Nm for torque, ± 0.5 bar for pressure, ± 0.1 °C for fluid temperature in the wheel and ± 1.0 °C for temperature in the chamber.

Experimental procedure

1 Continuous flow

The wheel is rotated at a constant peripheral velocity (1.0 m/s) as the temperature is reduced from about 60°C to 4°C at a given cooling rate. In the following, these experiments are referred to as continuous flow experiments. In condensate systems without emulsifiers added, a velocity of 1.0 m/s creates separated liquid phases (prior to hydrate formation). The phases are generally mixed at this velocity when black oil systems are used.

2 Start-up

The system is cooled as the wheel is rotating (peripheral velocity of 1 m/s) to about 30 °C before the wheel is stopped. The wheel is then cooled to a temperature of 4°C and kept constant for a period of minimum 12 hours. The wheel do not move during this period. Then the wheel is restarted and rotated at a constant peripheral velocity of 1.0 m/s for the rest of the experiment. These experiments are referred to as start-up experiments.

In order to minimize the number of adjustable parameters for the experiments, only one given cooling rate is used both for the continuous flow experiments and the start-up experiments.

Results and discussion

The hydrate inhibitor tested in this work is a commercially available kinetic inhibitor consisting of a blend of different polymer/surfactants.

In this specific study the inhibitor was tested in the high-pressure system using two different crude oils and two gas condensates. Also the presence of a coorosion inhibitor or a defoamer on the performance was investigated for some of the fluid systems. Results from 27 experiments performed in the flow simulator with the different hydrocarbon fluids are presented. A summary of the experimental conditions and observations from these experiments is given in **Table 1**. It should be stressed that the subcoolings given in the **Table 1** have been corrected for the actual salinity of the systems. The results are discussed in more detail below.

Condensate A

Impact of corrosion inhibitor

Based on the visual information from the experiments the addition of the corrosion inhibitor changed the physical properties of the system with respect to foaming tendency. No significant change of performance of the hydrate inhibiting properties was observed. In all the inhibitor experiments there was a considerable kinetic effect but there was a decrease in transporability at hydrate formation compared to the pure system.

Impact of salinity

The salinity of the aqueous phase in these experiments was varied from 0-3,5 wt%. Increased salinity resulted in an increased delay of hydrate formation from 80 min to 20 hours. Previous studies (1,3,5) have shown that the optimal salinity for this inhibitor is approx. 3,5 wt%. The improved performance is due to conformational changes in the polymer systems in the inhibitor. A salinity of 0,25 wt% corresponds to the actual salinity of the produced water from the field.

Impact of subcooling

As seen from **Table 1** the subcooling in the experiments are varied from 9°C to 13°C. At continuous flow mode an addition of 0.5 wt% of the hydrate inhibitor prevented hydrate formation at a subcooling of approximately 9°C for the test period of 36 hours when the salinity was 0,25 wt%. Also restarts after a shut-in of 12 hours was successfully carried out at this temperature, although there were hydrates present in the system. However, at subcoolings above 9°C, the hydrate inhibitor tested was not able to fully prevent the hydrate formation during continuous flow. But in all the experiments hydrate formation was delayed compared to experiments on the blank Condensate A fluid.

Condensate B

Impact of subcooling

Experiments were here performed with a inhibitor concentration of 0.5 wt% of the aqueous phase . As seen from exp. 15, no hydrate formation were observed in this system at a subcooling of 11°C at a pressure of 70 bar within an experimental time of 80 hours. When the subcooling was increased to 13°C, hydrate formation was observed after 9 hours. When increasing the pressure to 140 bar (exp.16) keeping the subcooling constant at 11°C, hydrates were formed after 6 hours, and the flowloop plugged 1 hour after hydrate initiation. In these experiments the aqueous phase contained 3.5 wt% NaCl.

Crude oil A

The kinetic inhibitor was tested with and without the presence of a corrosion inhibitor both in continuous flow experiments and in shut-in experiments. In exp. 17-20 also a defoamer was present in the system.

Impact of defoamer and corrosion inhibitor

From **Table 1** one can observe from experiments 17-26 that the prescence of the defoamer reduces the performance of the hydrate inhibitor dramatically. For practical purposes it does not work at all.

During the continuous flow experiments without the defoamer present a significant delay of the hydrate formation was observed both with and without the presence of the corrosion inhibitor. At a subcooling of 11°C the presence of the corrosion inhibitor improved the performance compared to the system with only the hydrate inhibitor present. Hydrate formation was not initiated during a period of 60 hours.

In the start-up experiments, however, the induction time was reduced. Hydrates were formed during the stagnant period (12 hours), and the wheel was plugged shortly after restart.

The transportability of the hydrates formed was better in the presence of the corrosion inhibitor. This is opposite to what was observed for condensate A, and it illustrates the importance of fluid effects when this kind of technology is considered for use.

Impact of subcooling

The subcooling in the experiments was varied from 7°C to 13°C. The chemical was not capable of fully preventing the hydrate formation in any of the experiments. However, at subcoolings below 10°C the hydrates formed were transportable.

Crude oil A

Impact of subcooling

During continuous experiments at a subcooling of 7.3°C and 0.5wt% of hydrate inhibitor no hydrate formation was observed for almost 10 hours. The formation rate was then very slow for 2 hours before it increased rapidly resulting in a viscosity increase of the system. No hydrate plugging was observed.

In the start-up at a subcooling of 9.5°C, hydrates started to form very slowly after start-up. After approx. 4 hours the formation rate increased drastically and flow problems were observed due to the high viscosity of the system. However, no "solid" hydrate plug was observed in the experiment.

Fluid and flow dependency

The inhibitor were tested in 4 different fluids with different composition and physicochemical properties. The performance of the inhibitor is different for all these fluids. It is not possible to extrapolate the results from one condensate to another, or one black oil system to another. It is known the parameters like aliphatic/aromatic ratio, amount and state of asphaltenes and resins and also wax content will influence on the performance, and these factors will always vary between different fluids.

Regarding the influence of flow properties it has for all the systems investigated been shown that stagnant conditions are more difficult to handle than continuous flow. This aspect should be investigated further and will be addressed more thoroughly in a forthcoming paper.

Summary and conclusions

A commercially available kinetic hydrate inhibitor in a high pressure flowing system at various conditions and for different fluid systems. Also the presence of other production chemicals have been addressed. The conclusions can be summarized as follows:

- the defoamer has a negative effect. It reduces the performance to nearly zero.
- the corrosion inhibitor results in an increased mixing/emulsification of the system. This might be a benefit in some systems (black oils) but not in others (condensates).
- the salinity is crucial for the performance.
- the maximum subcooling to be handled is in the range 7-11°C depending on the fluid system.
- the effect of the inhibitor is reduced at stagnant conditions.

The results strengthen the knowledge that results from one fluid system should not be extrapolated to another. These kind of chemicals have to be qualified for each given fluid before they can be applied at real conditions.

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Table 1: *Experimental conditions and observations from the experiments*

Exp.	Fluid	Inhibitor conc. (wt%)	Water cut (vol%)	Conc. of corr.inh. (ppm)	Salinity (wt%)	Mode	Sub cooling (°C)	Comments
1	Cond. A	0	20	-	0.25	Cont.	8.5	Hydrate formation started immediately and the pipe was plugged after 23 min.
2	Cond. A	0.50	20	800	0.25	Cont+start-up	13.0	Hydrate formation and plugging after 16 hours. Hydrate lumps and depositions at the window.
3	Cond. A	0.50	20	800	3.5	Cont+st.up	11.0	No hydrate formation observed during dynamic period. A hydrate plug formed during shut-in
4	Cond. A	0.50	20	800	3.50	Cont+start-up	11.0	A lot of foam in the condensate phase during dyn. conditions.. The foam broke down 5 hours after shut-in. Hydrate formation started after 9 hours. Plugged before restart.
5	Cond. A	0.50	20	-	0.25	Cont.	13.0	Foam observed in the condensate phase from start of experiment. Emulsification after 90 minutes and hydrate formation and plugging after 26 hours (dynamic conditions).
6	Cond. A	0.50	20	-	0.25	Cont+start-up	9.0	No hydrate formation observed during dynamic condition. 4 hours after shut-in hydrate formation started at interface growing into both condensate and aqueous phase. Loose hydrates. Smooth restart with minor depositions at the window.
7	Cond. A	0.50	20	-	0.25	Cont+start-up	11.0	Hydrate formation observed after 4 hours during dynamic conditions. Plugged before restart.
8	Cond. A	0.50	20	-	0	Cont.	10.5	No hydrate formation observed during the experimental time of 11 hours
9	Cond. A	0.50	20	-	0	Cont.	13.0	Hydrate formation and immediate plugging after 80 min.
10	Cond. A	0.50	20	-	3.5	Cont.	11	No hydrate formation observed for the experimental time of 25 hours.
11	Cond. A	0.50	20	-	3.5	Cont.	13	Hydrate formation and immediate plugging after 20 hours.
12	Cond. B	0	20	-	3.5	Start-up	14.5	Deposits and plugging within 11 min. after start of hydrate formation.
13	Cond. B	0.50	20	-	3.5	Start-up	13/15	No hydrate formation after 3 hours at 4°C. When temp. was lowered to 2°C rapid hydrate formation was initiated after 3.5 hours
14	Cond. B	0.50	20	-	3.5	Start-up	13	Rapid hydrate formation after 9.5 hours.
15	Cond. B	0.50	20	-	3.5	Cont.	11	No hydrate formation was observed within the experimental time of 80 hours
16	Cond. B	0.50	20	-	0	Start-up	11	Viscous emulsion after restart. Hydrate formation started 1.5 hours after restart.
17	Crude A	0	33	-	3	Start-up	13	Deposits at restart Plugging after 2 minutes.
18	Crude A	0.27	33	-	3	Start-up	13	Deposits at restart. Plugging after 1 minute
19	Crude A	0.27	33	-	3	Start-up	7	Hydrates formed 27 min. after restart Transportable hydrates but very viscous.
20	Crude A	0.50	33	-	3	Start-up	13	Hydrate deposits at restart. Plugging after 1 minute
21	Crude A	0	33	-	3	Start-up	10.5	Emulsion layer at the interface. Blocked 80 sec. after restart.

Exp.	Fluid	Inhibitor conc. (wt%)	Water cut (vol%)	Conc. of corr. inh. (ppm)	Salinity (wt%)	Mode	Sub cooling (°C)	Comments
23	Crude A	0.50	33	-	3	Cont.	11	Slow hydrate formation initiated after 7 hours. Formation rate increased later in the exp.
24	Crude A	0.50	33	-	3	Start-up	11.5	After stop of wheel the phases remained emulsified for 50 min. High formation rate 3 hours after start-up.
25	Crude A	33	0.50	800	3	Start-up	9	Droplets of water mixed in the oil phase. No hydrate formation for 68 hours. When subcooling was increased to 13°C the loop plugged.
26	Crude A	33	0.50	800	3	Start-up	11.2	Brown water phase during shut-in. Loop plugged 12 hours after restart.
27	Crude B	40	0	-	5	Start-up	7.6	Depositions and plugging 2 min. after start-up.
28	Crude B	40	0.5	-	5	Cont.	7.3	Slow hydrate formation initiated after 9.5 hours. More rapid formation after 11.5 hours and also large increase in viscosity.
29	Crude B	40	0.5	-	5	Start-up	9.5	No deposits observed at start-up, but slow hydrate formation observed. After 3.5 hours rapid hydrate formation occurs resulting in a very viscous system that nearly blocks the loop.

Figure 1: An illustration of the flow loop.

