FLOW ASSURANCE:

MICRO AND MACRO-SCALE EVALUATION OF LOW DOSAGE HYDRATE INHIBITORS

2002 – 2005 PROGRAMME

PROGRESS REPORT
June 2004 – November 2004
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Heriot-Watt Institute of Petroleum Engineering

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# TABLE OF CONTENTS

PERSONNEL AND SPONSORS ........................................................................................................ i

EXECUTIVE SUMMARY ........................................................................................................ ii

EXTENDED SUMMARY ........................................................................................................ iv

INTRODUCTION ...................................................................................................................... 1.1

VISUAL OBSERVATION BY MICROMODEL EXPERIMENTS .................................................. 2.1

KINETIC RIG EXPERIMENTS .................................................................................................. 3.1

HIGH PRESSURE VISUAL RIG EXPERIMENTS ................................................................. 4.1

HYDRATE NUCLEATION TESTS USING ULTRASONIC WAVES ........................................ 5.1

APPLICATION OF HELICAL TUBE MIXER IN EVALUATION OF ANTI-AGGLOMERANTS ................................................................. 6.1

APPENDIX A: EXPERIMENTAL FACILITIES AT THE CENTRE FOR GAS HYDRATE RESEARCH .......................................................................................... A.1

APPENDIX B: PRESSURE AND TEMPERATURE PROFILES OF THE TESTS IN THE KINETIC RIGS ................................................................................ B.1
The study was conducted in the Institute of Petroleum Engineering, Heriot-Watt University, under the direction of Professors B. Tohidi, A. Danesh, and A. C. Todd. Experimental and analytical works were carried out by Mr M. Arjmandi, Ms Z. Zain, Mr. R. Burgass, Dr. J. Yang, Mr J. Pantling and Mr C. Flockhart were in charge of manufacture and maintenance of the equipment.

The research project is supported by BASF, British Petroleum Plc., Clariant Oil Services, Gaz de France, OMV Aktiengesellschaft, TOTAL and the UK Department of Trade and Industry, which is gratefully acknowledged.
EXECUTIVE SUMMARY

The ongoing research programme is focused on the investigation of the mechanisms of Low Dosage Hydrate Inhibitors (LDHI) and the evaluation of their performance under different conditions. The main objectives of the research are:

- Development and application of new techniques for studying the mechanisms of hydrate inhibition by LDHIs.
- Evaluation of the performance of current LDHIs at various conditions.
- Guidelines on effective design and deployment of LDHIs
- Guidelines on screening of potential LDHIs using laboratory-based tests

The work in the last six months of the project can be summarised as:

- The morphologies of natural gas hydrates in the presence of a new base polymer (BASF advanced polymer) in different conditions were investigated by visual observations in the high-pressure micromodel set up. In comparison with PVCap, different morphology was observed. The result suggests that 5 volume% of the new base polymer is less effective than LUVICAP® in delaying hydrate growth.

- Characteristic behaviour of hydrate plugging in the presence of 0.5 mass% PVCap and a mixture of 0.5 mass% PVCap with 0.75 mass% propylene glycol propyl ether (PGPE) at the simulated pipeline conditions was investigated under flow conditions in high-pressure micromodel set up. In the presence of PGPE as a synergist to PVCap hydrate formed at higher degree of subcooling with slightly longer induction time. Furthermore, it took considerably longer time for the hydrate blockage as compared to PVCap without synergist and also the blank test.

- Experiments carried out in a kinetic rig on 5 volume% of BASF advanced polymer at different degrees of subcooling and in two hydrodynamic conditions; shut-in and flow (stirring) conditions. The results showed that for achieving the induction times longer than one day, the degree of subcooling should be less than 11.2 °C for natural gas system. At static conditions and same temperatures and pressures of those tests with mixing, similar induction times and lower rates of hydrate growth were observed.

- A known synergist chemical for PVCap, propylene glycol propyl ether was tested, at two different concentrations, in the presence of natural gas-water system
at different conditions in the kinetic rig. The results of the experiments showed the PGPE synergistic effect on the PVCap performance. Increasing the concentration of PGPE from 0.5 to 0.75 mass% improved its synergistic effect. It also improved PVCap performance in hydrate inhibition at static conditions by decreasing the rate of hydrate growth.

- The effect of a commercial corrosion inhibitor (Corrtreat 799 provided by Clariant Oil Services) on the performance of PVCap was studied by conducting a series of tests in a kinetic rig in the system of natural gas-water-1 mass% PVCap, in the presence and absence of corrosion inhibitor at different conditions. It appeared that corrosion inhibitor tested has a negative impact on the performance of PVCap under mixing and static conditions.

- A windowed kinetic rig was used to observe hydrate formation in natural gas–water system in the presence of 1.5 mass% ethylene glycol at static conditions. Rapid hydrate formation was observed to occur at the gas/liquid interface and then continue in the upper part of the cell. Gas bubbles appeared below the layer of growing hydrates as the water was drawn to the upper part of the cell. However, in methane-water system in the presence of ethylene glycol hydrates were seen to form a solid layer at the gas/liquid interface with small amount of hydrates growing above and below the interface.

- The hydrate growth patterns were observed for both structure II (natural gas) and structure I (methane) hydrates in the presence of an aqueous solution of the BASF advanced polymer in the windowed kinetic rig at static conditions. In the test with natural gas, hydrate formation was very rapid and the hydrates were seen to start forming at the gas/liquid interface and then to continue to form in the upper part of the cell. The hydrates did not form a continuous layer at the gas/liquid interface. In the test with methane the hydrate growth pattern was similar to that seen in the natural gas test.

- The effect of propylene glycol propyl ether on the hydrate growth pattern of hydrates formed from natural gas and methane in the presence of the BASF advanced polymer and PVCap was investigated in the windowed kinetic rig at static conditions. In the test with BASF advanced polymer in natural gas system,
the PGPE improved the polymer inhibition effect and less hydrate formed compared to the test in the absence of PGPE. The hydrate growth pattern was similar to the test with base polymer kinetic inhibitor alone. In the test with PVCap/PGPE the pressure time data showed a similar pattern to the BASF advanced polymer/PGPE test, however the growth pattern was different in that a layer of hydrates formed at the gas/liquid interface, hydrate growth continued in the upper part of the cell and gas bubbles appeared below the hydrate layer in the liquid phase.

- The nucleation and growth of hydrate in the presence of BASF advanced polymer in natural gas water system at static conditions was investigated in an ultrasonic set up. The results suggested that the advanced polymer inhibited hydrate formation almost completely before the catastrophic growth started, however, hydrates grew very rapidly once starting formation.

- The dependence of PGPE synergism effect upon its concentration was tested in the ultrasonic set up. The result showed that synergistic effect of PGPE on the performance of the both polymers (BASF polymer/PVCap) depends on its concentration, including delay of the catastrophic growth and reduction of hydrate formation rate.

- The application of a helical tube mixer in a kinetic rig for evaluation of anti agglomerants in condensate-water-natural gas systems was tested. The torque measurement results in the experiments carried out with two different types of condensate and natural gas-water systems in the presence and absence of an anti agglomerants showed promising results and applicability of the method.
EXTENDED SUMMARY

The ongoing research project started in September 2002 and is currently supported by 6 oil/gas and chemical companies and the Department of Trade and Industry (DTI). The research programme is focused on the investigation of the mechanisms of Low Dosage Hydrate Inhibitors (LDHI) and the evaluation of their performance under different conditions. The main objectives of the research include:

- Development and application of new techniques for studying the mechanisms of hydrate inhibition by LDHIs.
- Evaluation of the performance of current LDHIs at various conditions.
- Guidelines on effective design and deployment of LDHIs for deepwater applications
- Guidelines on screening of potential LDHIs using laboratory-based test procedures

In the last six months, the experiments were carried out in the kinetic rig to investigate the performance of a new base polymer kinetic inhibitor in different conditions, and the effect of a synergist chemical and a commercial corrosion inhibitor on the performance of PVCap and the base polymer kinetic inhibitor. Hydrate morphology in the presence of above inhibitors and synergist was investigated by visual observation in the high pressure micromodel rig. Characteristic behaviour of hydrate plugging with and without LDHI and/or synergist at the simulated pipeline conditions was investigated under flowing conditions in the high pressure micromodel set up. A high pressure windowed rig was used for visualisation of hydrate growth patterns in the presence of new inhibitor, the synergic chemical and ethylene glycol. The ultrasonic set up was used in studying nucleation and growth of hydrate with new inhibitor and the synergist. The application of a helical tube mixer in evaluation of anti-agglomerants in a kinetic rig was tested.

Micromodel Experiments

In the previous steering committee meeting, the experimental results carried out for natural gas and methane-water system in the presence of HI03-187 (containing PVCap and a synergist chemical) kinetic inhibitor was presented. The details of the results is documented in this report. The results showed that hydrate morphology with this...
inhibitor was in the form of thin patches of snowy crystals flakes which was similar to that observed in the bulk conditions of visual kinetic rig.

The experiments for natural gas-water system with 5 volume% of a new kinetic inhibitor (labelled as HT04-049 and containing the BASF new advanced polymer, water and a solvent) were carried out in high pressure micromodel set-up to study the mechanism of hydrate formation and crystal morphology in comparison with those of LUVICAP® (1 mass% PVCAP). Tests were carried out at two different pressures: 105 bar and 95 bar. At 105 bar, the system was cooled down step by step until hydrate formed at 2.5 °C (16 °C subcooling). As shown in Figure 1, initial hydrate formation started at the interface of gas and water and formed a thick non-transparent layer that outlined profile of gas bubbles. Hydrate formation was followed by a slow growth of small hydrate particles within the gas bubbles, which finally covered the whole gas bubbles profile. The hydrate particles turned into transparent and thin patches of crystals.

![Figure 1. Hydrate formation in Natural Gas-Water system in the presence of 5 vol% of HT04-049 at 105 bar, 2.5°C (16°C subcooling).](image)

In the experiment carried out at 95 bar and 4.2°C (13.7°C subcooling), hydrate formed only in the outlet tubing of micromodel and turned into transparent thin patches of crystal similar to those of test at 105 bar as shown in Figure 2. Comparison on hydrate morphology and crystal growth between HT04-049 and LUVICAP® showed that they are significantly different. In the presence of HT04-049 thin patches of hydrate crystals were formed, which were similar to those in the presence of HI03-24 (containing PVCap, and a synergist chemical) reported in the previous steering committee meeting (Figure 3). The natural gas hydrate crystals growth in the
presence of LUVICAP® and HT04-049 are compared. The result suggests that 5 vol% HT04-049 is less effective than LUVICAP® in delaying hydrate growth.

Figure 2. Hydrate formation in Natural Gas-Water System in the presence of 5 vol% of HT04-049 at 95 bar, 4.2°C (13.7°C subcooling).

Figure 3. Comparison of hydrate morphology for Natural Gas – Water system at 14°C subcooling with (a) 1 mass% PVCAP (b) 5 vol % HT04-049 (16°C subcooling) (c) 5 vol% of HI03-24

Characteristic behaviour of hydrate plugging with and without LDHI and/or synergist at the simulated pipeline conditions was investigated under flowing conditions. Tests with inhibitor were carried out using 0.5 mass% PVCap and a mixture of 0.5 mass% PVCap with 0.75 mass% propylene glycol propyl ether (PGPE). PGPE was selected as synergist chemical to study the effect of a known synergist on kinetic inhibitor performance and also its influence on hydrate morphology and plugging. The results (as shown in Table 1) suggest that PGPE enhances the performance of PVCap to inhibit hydrate formation and delay hydrate growth in flow conditions. In the presence of PGPE as a synergist to PVCap, hydrate formed at higher degree of subcooling with slightly longer induction time and more delay in hydrate blockage as compared to PVCap without synergist and also the blank test.
Table 1: Results of flow test by HP Micromodel

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hydrate formation temperature (°C)</th>
<th>Subcooling (°C)</th>
<th>Induction time at subcooling (hr)</th>
<th>Time for blockage (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>8</td>
<td>11</td>
<td>0.25</td>
<td>7.2</td>
</tr>
<tr>
<td>0.5 mass% PVCap</td>
<td>6</td>
<td>13</td>
<td>1.23</td>
<td>13.6</td>
</tr>
<tr>
<td>0.5 mass% PVCap + 0.75 mass% PGPE</td>
<td>4</td>
<td>15</td>
<td>1.63</td>
<td>23.8</td>
</tr>
</tbody>
</table>

Sequential pictures of progressive hydrate formation within capillary tubes for each tests are shown in Figure 4. The morphology for blank test at 11°C subcooling was in the form of a continuous non-porous solid hydrate, while in the presence of 0.5 mass% PVCap at 13°C subcooling, hydrate deposits initially appeared to be more porous and progressively turned to a non porous solid. In the presence of mixture 0.5 mass% PVCap and 0.75 mass% PGPE at 15°C subcooling, hydrate initially formed as a thin deposits and also solid hydrate in several parts of capillary tubes. Continuous flow of water and gas into the capillary tubes lead to buildup of solid hydrate and finally block the capillatry tubes.

Kinetics Rig Experiments

Three series of experiments were conducted using the kinetic rig. The first was to test a new base polymer (BASF advanced polymer labelled as HYTREAT 04-049) in order to find out the range of its applicability in different conditions. The performance of the inhibitor in terms of induction time was tested in different degrees of subcooling in natural gas-water system. The inhibitor was also assessed in two
hydrodynamic conditions; shut-in and flow (stirring) conditions. From the results of the tests on 5vol% of the new base polymer it appeared that for achieving the induction times longer than one day, the degree of subcooling should be less than 11.2 °C for natural gas system. At static conditions and same temperatures and pressures of those tests with mixing, similar induction times and lower rates of hydrate growth were observed. Figure 5 shows the pressure profiles of some of the mentioned tests in the kinetic rig in the presence and absence of mixing.

Figure 5. Pressure profiles of the tests in natural gas-water system in the presence of 5vol% kinetic inhibitor (HYTREAT® 04-049) in the kinetic rig in mixing and, static conditions.

As a part of comprehensive study on a known synergist chemical for PVCap, propylene glycol propyl ether was selected and its synergistic effect on PVCap performance, at two different concentrations, was tested in the presence of natural gas-water system at different conditions. The results of the experiments at the range of degrees of subcooling tested (13.9-14.1 °C), showed the PGPE synergistic effect on the PVCap performance. Increasing the concentration of PGPE from 0.5 to 0.75 mass% improved its synergistic effect (Figure 6). It also improved PVCap performance in hydrate inhibition at static conditions by decreasing the rate of hydrate growth (Figure 7).
Figure 6. Comparison of pressure profiles / induction times of the tests in natural gas-water system in the presence of 0.5mass% PVCap and different concentration of synergist in the presence of natural gas and water, at 600rpm.

Figure 7. Comparison of pressure profiles / induction times of the tests in natural gas-water system in the presence of 0.5mass% PVCap and 0.75mass% PGPE in the presence of natural gas and water at static conditions.
Finally, the effect of a commercial corrosion inhibitor (CorrTreat 799 provided by Clariant Oil Services) on the performance of PVCap was studied by conducting a series of tests in the system of natural gas-water-1 mass% PVCap in the presence and absence of corrosion inhibitor at different conditions. The tests results showed that in the presence of corrosion inhibitor, and 1 mass% PVCap, induction times longer than 1 day is achievable at degrees of subcooling less than 11°C. Considering the fact that in the absence of corrosion inhibitor similar induction times were achieved at 11.8°C subcooling, it appeared that corrosion inhibitor tested has a negative impact on the performance of PVCap. At static conditions, in the presence of corrosion inhibitor, again shorter induction times were observed at similar conditions of those tests in the absence of corrosion inhibitor.

**Experimental Measurements Made Using High Pressure Visual Rig**
Tests were conducted in a high pressure visual cell in order to observe hydrate growth patterns in static conditions. The first aim of the work was to find the effect of ethylene glycol at a low concentration (1.5 mass%) upon the hydrate growth patterns of natural gas and methane hydrates by comparison with distilled water. This was done in order to further investigate earlier work studying the growth pattern of hydrates in the presence of LUVICAP®. In tests with natural gas the ethylene glycol showed a significant influence in terms of the pressure/time data when compared with tests with distilled water and with LUVICAP® as shown in Figure 8. Rapid hydrate formation was seen to occur at the gas/liquid interface and then continue in the upper part of the cell. Gas bubbles appeared below the layer of growing hydrates as the water was drawn to the upper part of the cell as shown in Figure 9. In the tests with methane compared to tests with distilled water and with LUVICAP® the situation was different in that the pressure/time data with ethylene glycol was similar to that with distilled water as seen in Figure 10. Hydrates were seen to form a solid layer at the gas/liquid interface with small amount of hydrates growing above and below the interface as shown in Figure 11.
Figure 8. Pressure and time data for tests with natural gas in the presence of distilled water, natural gas in the presence of 1.5 mass% ethylene glycol, and natural gas in the presence of 2.5 mass% LUVICAP®.

Figure 9. Picture showing natural gas hydrate formation starting at the gas/water (1.5 mass% ethylene glycol) interface and continuing up the sapphire window. Hydrates can be seen forming on the surface of the bubble.
Figure 10. Pressure and time data for tests with methane in the presence of distilled water, methane in the presence of 1.5 mass% ethylene glycol, and methane in the presence of 2.5 mass% LUVICAP®.

Figure 11. Hydrate formation at the gas/water interface in the test with methane and an aqueous solution of ethylene glycol, hydrate continuing to grow into the liquid and gas phases.
The second aim of the work was to observe the hydrate growth patterns seen for both structure II (natural gas) and structure I (methane) hydrates in the presence of an aqueous solution of the BASF advanced polymer (labelled as HYTREAT® 04-049). This work was carried out in order to complement experimental measurements being made in other test rigs. In the test with natural gas, hydrate formation was very rapid as can be seen from the pressure and time data shown in Figure 12. The hydrates were seen to start forming at the gas/liquid interface and then to continue to form in the upper part of the cell drawing all of the water to the upper part of the cell. The hydrates did not form a continuous layer at the gas/liquid interface as shown in Figure 13. In the test with methane and HYTREAT® 04-049 there was sharp pressure drop when hydrates formed as shown in Figure 14 followed by a slower pressure decline with time. The hydrate growth pattern was similar to that seen in the natural gas test as shown in Figure 15.

Figure 12. Pressure and time data for test with natural gas in the presence of 5 volume% HYTREAT® 04-049.
Figure 13. Natural gas hydrate formation at the gas/water interface and on the cell window in the test with natural gas and an aqueous solution of HYTREAT® 04-049.

Figure 14. Pressure and time data for tests with methane in the presence an aqueous solution of HYTREAT® 04-049.
The final aim of this work was to investigate the effect of propylene glycol propyl ether (PGPE), as a known synergist chemical, on the hydrate growth pattern of hydrates formed from natural gas and methane in the presence of HYTREAT® 04-049 and LUVICAP®. This work was conducted to give additional information to tests being carried out in the other experimental rigs. In the test with natural gas the PGPE showed a significant influence upon the pressure/time data as shown in Figure 16. The outcome was that less hydrates formed from a pressure reduction point of view. The hydrate growth pattern was similar to the test with HYTREAT® 04-049 alone, an example is shown in Figure 17. In the test with LUVICAP®/PGPE the pressure time data showed a similar pattern to the HYTREAT® 04-049/PGPE test as shown in Figure 18. The growth pattern was different in that a layer of hydrates formed at the gas/liquid interface, hydrate growth continued in the upper part of the cell and gas bubbles appeared below the hydrate layer in the liquid phase. A layer of hydrates formed on the surface of the bubbles as shown in Figure 19.
Figure 16. Pressure and time data for tests with natural gas in the presence of aqueous solutions of HYTREAT® 04-049/PGPE and HYTREAT® 04-049.

Figure 17. Hydrate formation in the upper part of the cell gas/water in the test with natural gas and an aqueous solution of HYTREAT® 04-049/PGPE.
Figure 18. Pressure and time data for tests with natural gas in the presence of an aqueous solution of LUVICAP®/PGPE.

Figure 19. Hydrate formation at the gas/liquid interface, in the upper part of the cell and on the surface of gas bubbles below the interface in the test with natural gas and an aqueous solution of LUVICAP®/PGPE.

**Hydrate Nucleation Tests Using Ultrasonic Waves**

In last six-month period of the project, June 2004 – Nov. 2004, nucleation tests have been further conducted by means of the ultrasonic rig, in four groups of tests. In the first group of tests, the BASF advanced polymer was tested. Then the synergistic
effect of Propylene Glycol Propyl Ether (PGPE) on the performance of both PVCap and the advanced polymer was also investigated. The dependence of PGPE synergism effect upon its concentration was tested in the third group of tests. Finally, the kinetic feature of hydrate formation in the presence of PGPE was examined.

The test results show that the inhibition feature of BASF advanced polymer (HYTREAT 04-049), typically in Figure 20. The advanced polymer inhibited hydrate formation almost completely before the catastrophic growth started, which gives longer induction time. However, hydrates grew very rapidly once starting formation.

Figure 20. Inhibition feature of HYTREAT 04-049 (5vol%), under 12 °C of subcooling.

Figure 21. Inhibition feature of PVCap (0.5 mass%), under 15 °C of subcooling
By comparison, as can be seen in Figure 21, PVCap mainly hindered hydrate growth rather than nucleation, which gives shorter nucleation time but significantly lower hydrate growth rate. As can be seen in Figure 22, PGPE as a synergist can significantly improve the performance of both HYTREAT 04-049 and PVCap. Addition of 1.5 mass% of PGPE to 5 vol% of BASF advanced polymer increased the induction time by 4 hours under 15 °C of subcooling (Figure 22(a)), and by 29 hours under 12 °C.

Figure 22(a) 1.5 mass% of PGPE and 5 vol% of the BASF advanced polymer.

Figure 22(b) 0.75 mass% of PGPE and 0.5 mass% of PVCap

Figure 22. Addition of PGPE as a synergist can significantly improve the performance of both HYTREAT 04-049 and PVCap
Addition of 0.75 mass% of PGPE to 0.5 mass% of PVCap increased the induction time by 6 hours under 15 °C subcooling, and delayed of the catastrophic growth by more than 36 hours (Figure 22(b)).

Finally, it was found that synergistic effect of PGPE on the performance of the both polymers certainly depends on its concentration, including delay of the catastrophic growth and deduction of hydrate formation rate, and that PGPE alone may have some hydrate inhibition effect under static conditions.

**Application of Helical Tube Mixer in Evaluation of Anti-Agglomerants**

In the previous progress reports the experimental facilities in the Heriot-Watt University for evaluation of anti-agglomerants were detailed. In addition to application of Glass Micromodel set up, torque measurement in a kinetic rig was used for evaluation of anti-agglomerants. However, it was observed that in some tests, after hydrate formation, the torque was decreased because of movement of hydrate particles towards the rig wall due to centrifugal force of the paddle type impeller. In last six months of the project, the application of a helical tube mixer in a kinetic rig for evaluation of anti-agglomerants in condensate-water-natural gas systems was studied. The first series of tests conducted in natural gas-water system at three different rates of mixing (100, 200 and 400 rpm). In all the experiments, the test started at around 120 bar and 34 °C and the system was cooled down to 3-4 °C to form hydrate. After some time the system was heated up to 34 °C to dissociate the hydrates. During the tests the pressure, temperature and torque profiles were recorded. On the basis of those tests, rate of mixing 400 rpm was found to be better for torque measurement than the two other mixing rates because at 100 rpm the mixing was poor and hydrate formation was slow and at 200 rpm the torque reduction after hydrate formation was considerable. Figure 23 presents the pressure, temperature and torque profiles of experiment with 400 rpm.
In the second series of experiments, which were carried out at similar conditions and with a rate of mixing of 400 rpm, a solution of 33 volume % water in a North Sea field natural gas condensate (labelled as LTB98-1-C) was used in the presence and absence of an anti-agglomerant (HT03-186 supplied by Clariant Company). The first test carried out in the absence of AA. The profiles of the first test are shown in Figure 24. As seen, in test with condensate, after hydrate formation the torque is stable while in the test with natural gas-water (Figures 23) the torque was decreasing slowly. Good repeatability of experiment was observed. It was also noticed that at similar test conditions, in the presence of a condensate phase less hydrate formed than that in NG-water test (compare Fig.23 with Fig. 24). This may be attributed to natural inhibition of condensate phase. The result of the test in the presence of AA is presented in Figure 25. It was noticed that although the amounts of hydrate formed in the presence of anti-agglomerant was much higher than that tests without AA (Fig.24), the torque values after hydrate formation in the presence of anti-agglomerant appeared to be around 20% less than that of in the absence of AA (for the tests conducted on this fluid system).
Figure 24. Pressure, temperature and torque profiles for Condensate (LTB98-1-C) NG-water system, rpm=400.

Figure 25. Pressure, temperature and torque profiles for Condensate (LTB98-1-C) NG-water and 2.5 vol% HT03-186, rpm=400.

In the third series of tests, another condensate (East Frigg Field Natural Gas Condensate) in the presence and absence of anti-agglomerant was used. Again after hydrate formation in the presence of AA, lower torque values were observed in comparison with test without AA.
CHAPTER 1
INTRODUCTION

1.1. BACKGROUND
The economic risks involved in developing offshore and deepwater reservoirs demand cost effective methods and techniques for providing flow assurance solutions. The use of long tiebacks for transporting unprocessed well-stream could play an important role in the economical development of many deepwater and marginal fields (Bringedal, et al. 2000). A major concern with these subsea pipelines and production facilities is the possibility of flow restriction and blockage due to hydrate formation, which can lead to serious operational and safety problems. The cost of failure can be very high because of the high remediation cost and significant loss of revenues (Fu, B. et al. 2002).

Hydrates are crystalline, ice-like solids that form when gas molecules are trapped in hydrogen-bonded water cages under high pressure and low temperature conditions. These conditions are very typical for offshore operations. Conventional chemical treatments for preventing of hydrate formation are through one, or a combination, of methods such as: dehydration; insulation/heating; suitable operational practises; or injection of various chemical inhibitors (e.g. methanol or glycol). Conventional thermodynamic inhibitors are a major tool in current hydrate prevention strategies, but must be used in large volumes, e.g., up to 50 wt% methanol in the water-rich phase. This imposes severe capital and operational costs (Grainger M. et al. 1998).

Indeed, it is recognised that the cost of all the conventional hydrate prevention strategies can be prohibitively expensive for new deepwater developments and do shorten the economic life of mature assets.

In the past decade, a new group of non-thermodynamic chemical inhibitors has been developed which has received considerable attention from the industry. A number of laboratory studies and field trials have been reported in literature (Grainger M. et al. 1998, Mitchell G.F. et al., 1999, Argo C.B.. et al., 2000, Lovell D., et al., 2002. ). These chemicals do not shift the thermodynamic phase boundary of hydrate formation, but interfere with the process of hydrate formation by means of a number
of mechanisms proposed by several researchers (Sloan, E.D., 1998, King Jr H.E. et al., 2000, Koh C.A.et al., 2002, Storr M.T., et al., 2002, Makogon T. et al., 2002). Because the effective dosage for these new chemicals is much lower than those required for thermodynamic inhibitors, the new inhibitors are known as low dosage hydrate inhibitors (LDHI). LDHIs are typically divided by different active mechanisms such as, anti-agglomerants (AA) and kinetic hydrate inhibitor (KHI). The anti-agglomerants are based on preventing the agglomeration and deposition of hydrate crystals so that a transportable hydrate slurry could be formed (Frostman L.M. et al. 2000). Current anti-agglomerant inhibitors are generally used in the presence of an oil phase.

Like many other crystallisation process, the formation of gas hydrate also involves two processes: nucleation and crystal growth. It is speculated that the effect of a kinetic inhibitor (long polymer chains) is to interfere the nucleation process and/or prevent the crystal growth after its nucleation (Sloan, E.D., 1998, King Jr H.E. et al., 2000, Koh C.A.et al., 2002, Storr M.T., et al., 2002, Makogon T. et al., 2002). Therefore, effective kinetic inhibitors should either delay/prevent hydrate nucleation, and/or delay the catastrophic growth of hydrate volume and provide a hydrate induction time exceeding the water residence time in the pipeline. The induction time is defined as the duration beginning when the system falls into the hydrate-forming region until the onset of hydrate formation. It can be the most important parameter to evaluate the performance of a kinetic inhibitor. The LDHIs developed over the past decade have provided proof of concept, but still need considerable development before they can be adopted in many applications. The mechanism of LDHIs is still far from comprehensive apart from the adsorption theory (Sloan, E.D., 1998, King Jr H.E. et al., 2000, Koh C.A. et al., 2002). Three problems in particular arise: the extent of subcooling induced, the operating pressure, and the environmental acceptability. The current generation of LDHIs allow only 10–12 °C subcooling at medium pressure conditions whereas about 20 °C at high-pressure conditions is needed in many applications. There is still a need for the development of LDHIs suitable for high degree of subcooling and for high pressures. The performance of current LDHIs at various conditions has not been fully investigated. There has been rare information regarding hydrate formation and the mechanism and effect of LDHIs at micro-scales.
In response to the interests from the industry, the Centre for Gas Hydrate Research at Heriot-Watt University has extended its long-established hydrate research activities to the current project; **Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors.** The objective of this study is to gain better understanding of gas hydrate formation and inhibition mechanisms using LDHIs both in micro and macro-scales, principally by the application of a glass micromodel set-up in combination with a conventional hydrate kinetic rig using a large stirred tank (Tohidi, B. et al., 2001, Yang J., et al., 2000). The micromodel set-up will be used to gather data on hydrate crystal size and hydrate-fluid segregation. The kinetics rig is useful for evaluating the performance of inhibitor for industrial applications. It is proposed to study various fluid systems, including, CO₂, methane, natural gases, gas condensate and oil systems. The information generated in this work will be used to identify/design more effective low dosage hydrate inhibitors and/or deployment procedures for deepwater applications.

1.2. CENTRE FOR GAS HYDRATE RESEARCH-HWU

In response to the interest indicated by the industry, the Department of Petroleum Engineering at Heriot-Watt University extended its research activity to hydrates in 1986. A number of research projects, mainly in addressing gas hydrate problems in subsea pipelines, have been conducted since then, resulting in the development of experimental equipment, novel test procedures, and prediction models. In June 2000, the research group was successful in securing a Research Development Grant from the Scottish Higher Education Funding Council to establish a Centre for Gas Hydrate Research at Heriot-Watt University.

The Centre was formally established in February 2001. The funding enabled us to refurbish the hydrate laboratory and extend our research activities to various applications of gas hydrates, by employing new staff and forming a multi-disciplinary research team with expertise in Chemical and Petroleum Engineering, Geology, Physics, and Chemistry.

The 17-person strong research group is active in a number of various aspects of gas hydrates, such as:

- Flow assurance, avoiding hydrate and wax problems in subsea transfer lines
• Kinetics of hydrate formation and dissociation
• Design and evaluation of low dosage hydrate inhibitors
• Storage and transportation of oil and gas using hydrate technology
• CO₂ separation and sequestration
• Gas hydrates in marine sediments
• Positive applications of gas hydrates

The results of the studies have been well documented in more than 100 publications.

The experimental facilities, in two well-equipped laboratories, include (please refer to Appendix A for a complete list of the experimental equipment):

• Two rigs for hydrate phase equilibria and compositions at bulk conditions (700-2000 bar)
• Two Quartz Crystal Microbalance (QCM) rig for hydrate and wax equilibria (up to 400 bar)
• High pressure visual wax-hydrate rig (500 bar)
• Porous media rig (400 bar)
• Two micromodel Rig for visual observation of hydrates in micro-scale (80-400 bar)
• Kinetics Rigs-1 to 6 and (300 to 700 bars), one under construction
• Two ultrasonic rigs (400 bar), one under construction
• Combined visual, ultrasonic, and QCM rig (400 bar), convertible to micromodel rig, under construction
• “salting out” rig for salt solubility in mixtures of water and organic inhibitors
• Freezing point and boiling point rigs
• GC/MS

The hydrate theoretical studies have resulted in a reliable thermodynamic model, which is capable of predicting phase behaviour, including hydrate phase boundaries and flash calculations. Comparative studies with other commercially available packages have demonstrated the reliability of the developed thermodynamic model (Tohidi et al., 1997). For this reason, our gas hydrate prediction software (HWHYD)
has been selected by a number of major companies for use in their operational and research activities.

The Centre provides support to the industry through 2 JIPs, technical studies, short courses, and supplying computer software. The main strength of the Centre is based on its dedicated multi-disciplinary research team, purposely built equipment in our workshop, and excellent laboratory facilities.

1.3. KINETIC HYDRATE INHIBITORS
The background to the development of kinetic hydrate inhibitors is well documented (Sloan, E.D., 1998). Initially, alkylarylsulfonic acid and its salt, alkyl glycocides, tyrosine derivatives, and some surfactants have been patented as kinetic inhibitors. The finding of polymeric materials, such as polymers with an amide group (-N-C=O), has made the so-called first generation of KHIs available for commercial applications (Sloan, E.D., 1998, Fu, B. et al., 2002). Polymers used in the first generation KHIs include homopolymers, such as polyvinylpyrrolidone (PVP) and polyvinylcaprolactom (PVCAP), and their copolymers. The performance of the initial inhibitor formulation with single polymer component was not very satisfactory. Therefore, the second-generation inhibitors have been formulated and commercialised for industrial applications. These products are mainly new formulations based on PVP and PVCAP and their derivatives to enhance product performance. Some modifications on polymer structure, molecular weights, polymerisation process, and adding good synergists have been made to increase the inhibitor performance (Bringedal, B., 2000, Frostman L.M. et al., 2001, Bakeev K.N. et al, 2000).

Limited tests at our laboratory and other unpublished data have shown that the second generation KHIs could handle subcooling up to 13 °C with at least 48 hours induction time, but their performance could be greatly affected by the presence of other compounds in the system, such as gas composition, liquid hydrocarbons, corrosion inhibitors or other chemicals. They are also sensitive to pressure and temperature in different circumstances.

1.4. MECHANISMS OF KINETIC INHIBITORS
Despite the technical achievements offered by the KHIs, the mechanism of inhibition remains unclear. This has been argued whether the polymers act on the surfaces of an
already exiting hydrate crystal or whether they associate in some manner with hydrate-forming constituents while still in solution. The adsorption theory was supported by studies using small-angle neutron scattering (SANS) techniques and molecular simulations (King Jr H.E. et al., Storr M.T., et al., 2002, Makogon T. et al., 2002). However, whether and how the polymers delay or enhance hydrate nucleation is still not clear (Koh C.A. et al., 2002). The effect of synergists, and other compounds on the performance of these KHI s remains unexplored.

In this project, the mechanisms of LDHIs, with particular emphasis on KHI s, will be investigated using the high-pressure glass micromodel combined with other techniques such as ultrasonic, visual and non-visual high-pressure kinetic rigs.

1.5. RESEARCH OBJECTIVES
The research objectives could be summarised as:

• Gain better understanding of the process gas hydrate formation in gas and oil systems using the high pressure (400 bar) glass micromodels, and investigate the mechanism of gas hydrate inhibition by LDHIs using visual capabilities of glass micromodels and other analytical techniques

• Upscale and repeat the micromodel tests using stirred tank type high pressure kinetics rig (up to 700 bar), and evaluate the performance of various LDHIs under different operating conditions.

• Study the effect of other factors on the LDHI performance, including presence of liquid hydrocarbon, gas compositions, gas/water ratio and gas hydrate structure.

• Use the information generated above in improving the design, formulation and/or deployment of LDHIs.

• Test new chemicals and new formulations to enhance the performance of current and new LDHIs supplied by the sponsors.

• Guidelines on effective design and deployment of LDHIs for deepwater applications

• Guidelines on screening of potential LDHIs using laboratory-based test procedures

This project is supported and participated by sponsors from chemical manufacturers (chemical company), inhibitor providers (service company), inhibitor users (oil companies) and the DTI. This will provide a unique opportunity for the project to be
steered corresponding to the industrial demand closely, and ensure a rapid materialisation of the research outputs.

1.6. PROGRESS REPORT

A technical steering meeting will be held twice a year to review the project work programme and progress. Every six months a project report will be produced and circulated to the sponsors prior to the six monthly meeting.

In the last six months, the experiments were carried out in the kinetic rig to investigate the performance of a base polymer kinetic inhibitor in different conditions, and the effect of a synergist chemical and a commercial corrosion inhibitor on the performance of PVCap and the base polymer kinetic inhibitor. Hydrate morphology in the presence of above inhibitors and synergist was investigated by visual observation in the high pressure micromodel rig. A high pressure windowed rig was used for visualisation of hydrate growth patterns in the presence of new inhibitor, the synergic chemical and ethylene glycol. The ultrasonic set up was used in studying nucleation and growth of hydrate with new inhibitor and the synergist. The application of a helical tube mixer in evaluation of anti agglomerants in a kinetic rig was tested.

Chapter 2 presents the results of the micromodel experiments carried out on a new base polymer kinetic inhibitor in natural gas systems. In this chapter the characteristic behaviour of hydrate plugging in the presence of PVCap and a mixture of PVCap and a synergist in flow conditions is also presented. Chapter 3, presents the results of the experiments carried out on the mentioned kinetic inhibitors in the presence of a synergist chemical and a corrosion inhibitor in the kinetic rigs to evaluate their performance in different bulk conditions. Visual observations of hydrate formation in natural gas-water and methane water systems in the presence of new inhibitor, synergist chemical and ethylene glycol, using a windowed rig, at static conditions, are presented in chapter 4. Chapter 5 describes the results of the tests in ultrasonic set up to investigate hydrate nucleation and growth in the presence of new kinetic inhibitor and the synergist chemical. The results of the tests for evaluation of an anti agglomerant by torque measurement in a kinetic rig are presented in Chapter 6.
REFERENCES:


Lovell D., Pakulski M., “Hydrate Inhibition in Gas Wells Treated with Two Low Dosage Hydrate Inhibitors”, SPE paper 75668, presented at the SPE Gas Technology Symposium held in Calgary, Canada, 40 April-2 May, 2002.


CHAPTER 2
HIGH PRESSURE MICROMODEL EXPERIMENTS

2.1. INTRODUCTION

In the previous six months we had focused on studying the effect of various PVCap based kinetic inhibitors with synergist chemical (i.e. HI03-04, HI03-22 and HI03-187) on the gas hydrate crystal morphology and their particles size. The aim was to understand the basics of the gas hydrate formation and growth for methane gas and natural gas water system at different conditions and the mechanism of inhibition by low dosage hydrate inhibitors. Studies were performed at static conditions using visual observation in high-pressure micromodel with 5 vol% of inhibitor concentration.

The test carried out at 17°C subcooling for natural gas-water system with HI03-22 (PVCap with synergist) inhibitor showed that hydrate formed as thin patches of flaky crystals. This inhibitor appeared to be more effective in delaying hydrate formation as compared to PVCap (without synergist). This results also supported by the kinetic rig and ultrasonic test results at static condition. In the presence of HI03-24 inhibitor, it was observed that different degrees of subcooling (11.4 – 14.4°C) lead to different mechanisms of hydrate formation and morphologies. The hydrate particles turned to a smooth whiskery hydrate crystals in water phase and a thread like hydrate crystals in the gas phase. The results also suggested that HI03-24 inhibitor was not as effective as PVCap in preventing hydrate formation from dissolved gas in water phase.

The different hydrate morphologies in natural gas-water system formed in the presence of different kinetic inhibitors (all PVCap-based with different synergists) at similar degrees of subcooling were compared. While the hydrate morphologies for the systems without inhibitor and the systems with PVCap are not significantly different, it was observed that in the presence of HI03-24 and HI03-22 the morphology is mainly patches of very thin crystal flakes and small hydrate particles respectively. This suggests that the synergist chemicals have changed hydrate morphology and particle size for the same system. Morphologies of hydrate crystal at similar degree of subcooling for natural gas-water and methane-water systems were

2.1
The results suggested that the synergist chemicals have changed hydrate morphology and particle size for different hydrate structure. Finally, results for another inhibitor, HT03-187 supplied by Clariant Oil Services, was presented during the meeting but will be documented in this report. The hydrate morphology for this inhibitor was in the form of thin patches of snowy crystals flakes which was similar to that observed in the bulk condition of visual kinetic rig.

In this phase of project, experiments were divided into two parts. The first part was investigating the effect of 5 vol% of the BASF advanced base polymer for natural gas-water system at static condition using pore structure micromodel similar to the previous reported tests. The second part was investigating the system under flowing condition using multichannel flow conduit. The objective of this work was to establish procedure incorporating into existing in-house laboratory protocol (HP cell rig, Ultrasonic, Visual rig, static Visual HP Micromodel) for investigating kinetic of hydrate formation, inhibition and evaluating performance of LDHI. During flow test, characteristic behaviour of hydrate plugging with and without LDHI and/or synergist at simulated pipeline condition was investigated. Experiments were performed with natural gas-water system with and without kinetic inhibitors. Tests with inhibitor were carried out using 0.5 mass% polyvinylcaprolactam (PVCap) and a mixture of 0.5 mass% PVCap and 0.75 mass% Propylene glycol propyl ether (PGPE). PGPE was selected as synergist chemical to study the effect of known synergist on kinetic inhibitor performance and also its influence on the morphology of hydrates.

The following sections of the report describe experimental procedure for flow test and the results for natural gas-water system and methane–water system in the presence of HT03-187. The natural gas-water system in the presence of the BASF advanced base polymer and results on testing under flow conditions are reported. Finally the summary of results is included in the last section of the report.

2.2. EXPERIMENTAL PROCEDURE

The experimental procedure for static test using pore structure micromodel was described in detail in the previous progress report (March – November 2003). This section will only focus on procedure related to flow test. A pore structure glass micromodel was replaced with a multichannel flow conduit glass micromodel shown
in Figure 2.1. The micromodel, filled with deionised water, was initially pressure tested step by step up to 280 bar at 20°C for more than 24 hours. Then the system temperature was reduced to the desired test temperature and allowed to stabilise before saturating with test fluids.

Figure 2.1 Multichannel flow conduit and experimental set-up

Tests under flowing conditions were conducted for natural gas-water system in the presence of 0.5 mass% polyvinylcaprolactam (PVCap) supplied by Clariant Oil Services and a mixture of 0.5 mass% PVCap with 0.75 mass% Propylene glycol propyl ether (PGPE). Aldrich supplied PGPE, with 99% purity.

The deionised water (dyed with methyl blue) with or without kinetic inhibitor was saturated with natural gas at 103 bar in high-pressure cylinders. The cylinder content was shaken several times to promote gas dissolution in the water and it was left overnight for equilibrium. About 20 cc of this presaturated solution was charged into the sample cylinder of micromodel set-up at constant pressure using HPLC pump. Another sample cylinder was filled with natural gas at the desired pressure of the test.
Deionised water inside the system was then displaced with presaturated solution at constant pressure and allowed to equilibrate at desired temperature and pressure.

Flow test began by simultaneously injecting presaturated solution and natural gas at constant rate of 0.1 cc/hr into the system through outlet side of micromodel using high-pressure quizix pump. Pressure inside the micromodel was maintained at 103 bar by backpressure regulator attached at the inlet side. The formation of hydrate was visually observed and recorded accordingly. The measured and observed parameters are nucleation time (induction time), characteristic of hydrate build-up and deposits in the glass wall (no deposit, traces, thin hydrate layer, large deposits) and changes in differential pressure across micromodel due to hydrate blockage. The nucleation time (induction time) was measured from the time when the injection started at stabilised conditions of pressure and temperature.

2.3. RESULTS AND DISCUSSION

2.3.1. In the presence of HI03-187

Test was carried out in the presence of 5 vol% HI03-187, another PVCap base polymer with a synergist, at 90 bar (13.9°C subcooling) with natural gas-water system. In this test, the temperature of the system was reduced to 4.1°C and hydrate formed after about 80 hours of induction time. As shown by still pictures in Figure 2.2, it was observed that hydrate formed following gas bubbles profile (Figure 2.2(b)). The non-transparent hydrate particles in the gas bubbles profile turned to white (translucent), thin patches of hydrate crystals with snowy and flake type morphology (Figure 2.2 (c)) after 24 hours in the system. The morphology indicated a more porous hydrate, less packed and with disorder in the structure leading to higher porosity. In comparison with PVCap, this new PVCap base polymer with synergist seems to be far more effective in preventing hydrate formation based on longer induction time for hydrate formation (compared to PVCap with 8 hrs induction time at 14°C subcooling). This inhibitor appeared to be very effective in preventing hydrate formation in water phase for natural gas-water system.
Another test was carried out for methane-water system at 117 bar (13.6°C subcooling). The system temperature was reduced step by step from 4.3°C to 3°C within 92 hours. Then the temperature was set at 1.6°C for 48 hrs and hydrate did not formed. When the system temperature was further reduced to 0.7°C, hydrate immediately formed within the gas bubbles with non-transparent hydrate particles as shown in Figure 2.3. After 24 hours of hydrate formation, the edge of hydrate particles turned to translucent hydrate crystal forming more order crystal morphology (Figure 2.3 (c)). Finally the hydrate crystal formed shells inside the gas bubble profile and water molecules remained in the middle. Similar to natural gas–water system, this inhibitor prevents hydrate formation in water phase at this condition. Based on these results, it is clear that HI03-187 kinetic inhibitor has also changed hydrate morphology for different hydrate structure at similar degree of subcooling.

Figure 2.2. Hydrate formation in Natural Gas-Water System in the presence of 5 vol% HI03-187 at 90 bar, 4.1°C (13.9°C subcooling).

Figure 2.3. Hydrate formation in Methane -Water System in the presence of 5 vol% HI03-187 at 117 bar, 0.7°C (13.6 °C subcooling).
2.3.2. In the presence of the BASF advanced base polymer

The tests for natural gas-water system with 5 vol% of new advanced base polymer kinetic inhibitor were conducted to study the mechanism of hydrate formation and crystal morphology in comparison with Pvcap (1 mass%). The new KHI (labelled as HT04-049) was supplied by Clariant Oil Services, which is composed of the BASF new advanced polymer, water and a solvent. In order to make comparison, similar procedure was adopted as in previous experiments.

The inhibitor solution (presaturated with natural gas) and natural gas were charged into the micromodel at 105 bar. The system was cooled down to 4°C (14.5°C subcooling) and hydrate did not form after 42 hours. The temperature was further decreased step by step until it formed at 2.5 °C (16 °C subcooling). As shown in Figure 2.4, initial hydrate formation initiated at the interface of gas and water forming a thick non-transparent layer outlining profile of gas bubbles (Figure 2.4(b)). Then a slow growth of small hydrate particles appeared within the gas bubbles. After about 24 hours (Figure 2.4(c)), most of the gas bubbles profiles were covered with these hydrate particles and at some locations they turned into transparent and thin patches of crystals. The growth of hydrate crystals completed after 72 hours as shown in Figure 2.4(d). The sequential still pictures taken during hydrate dissociation (Figure 2.5) showed clearly how hydrate dissociated into tiny hydrate particles within gas bubbles as observed during initial hydrate formation. At static condition there is still remnants of hydrate particles left within gas bubbles, which may require longer time to dissociate at temperature above dissociation temperature.
Figure 2.4. Hydrate formation in Natural Gas-Water System in the presence of 5 vol% of HT04-049 at 105 bar, 2.5°C (16°C subcooling).

Figure 2.5. Hydrate dissociation in the presence of 5 vol% of HT04-049 at 107 bar

In another experiment carried out at 95 bar and 4.2°C (13.7°C subcooling), hydrate formed in the outlet tubing of micromodel that turned into transparent thin patches of
hydrate crystal (Figure 2.6). However, it was observed that hydrate did not grow further inside the micromodel. After leaving the system for 24 hours, temperature was further reduced and more hydrate started to form in the pore structure of micromodel at 2.6°C (15.4°C subcooling) as shown in Figure 2.7. It is interesting to note that the mechanism of initial hydrate formation and morphology was similar to that at 13.7°C subcooling. There was still remaining gas bubbles and water, which did not convert to hydrate. Larger driving force (higher degree of subcooling) maybe required to covert the remaining water and gas molecules to hydrate.

![Figure 2.6](image)

(a) Before hydrate formation

(b) 2 hrs after hydrate formation  (c) 24 hrs after hydrate formation

Figure 2.6. Hydrate formation in Natural Gas-Water System in the presence of 5 vol% of HT04-049 at 95 bar, 4.2°C (13.7°C subcooling).
Figure 2.7. Hydrate formation in Natural Gas-Water System in the presence of 5 vol% of HT04-049 at 95 bar, 2.6°C (15.4°C subcooling).

2.3.3. Comparison on Hydrate Crystal Morphology and Growth

As reported in the last progress report, different hydrate morphologies in natural gas-water system formed in the presence of different kinetic inhibitors (all PVCap-based with different synergists). In this section, the comparison is made between the new BASF advanced base polymer and PVCap based polymers. As shown in Figure 2.8, while morphology in the presence of PVCap based polymer and blank sample without inhibitor exhibits mainly continuous solid hydrate crystals, in the presence of HT04-049 it exhibits thin patches of hydrate crystals. The transparent thin patches hydrate crystal observed was similar to the one in the presence of HI03-24 (containing PVCAP and a synergist chemical) at 14°C subcooling (Figure 2.8 (d)).

The natural gas hydrate crystals growth in the presence of PVCap and HT04-049 are compared. Based on still pictures shown in Figure 2.9, in the presence of PVCap, the hydrate crystals have not turned to translucent (more perfect structure) after passing 72 hours from the first hydrate particles formation. On the contrary, all hydrate crystals turned into translucent (their final stage in structural formation) in the presence of HT04-049 at similar degree of subcooling after passing 24 hours of hydrate formation. This suggests that 5 vol% HT04-049 is less effective than 1 mass% PVCap in delaying hydrate growth.
Figure 2.8. Comparison of hydrate morphology for Natural Gas – Water system at 14°C subcooling (a) Without inhibitor (b) With 1 mass% PVCap (c) With 5 vol% HT04-049 (16°C subcooling) (d) With 5 vol% of HI03-24

Figure 2.9. Comparison of hydrate growth for Natural Gas – Water system for (a) 1 mass % PVCap at 14°C subcooling (b) 5 vol% HT04-049 at 13.7°C subcooling
2.3.4. Testing under flowing conditions

The objective of this work was to establish a new procedure incorporating into existing in-house laboratory protocol for investigating kinetics of hydrate formation, inhibition and evaluating performance of LDHI under flowing condition. During flow test, characteristic behaviour of hydrate plugging with and without LDHI and/or synergist was investigated.

The experiments were conducted for natural gas-water system in the presence of 0.5 mass% polyvinyl caprolactam (PVCap) and a mixture of 0.5 mass% PVCap with 0.75 mass% Propylene glycol propyl ether (PGPE). PGPE was selected as synergist chemical to study the effect of known synergist on kinetic inhibitor performance and also its influence on hydrate morphology and plugging. This combination of inhibitor and concentration was selected based on series of tests performed in kinetic rig and ultrasonic rig in bulk and static condition. PGPE, a non-toxic chemical, was reported to be the second best glycol ether solvents acts as synergist to PVCap and VC-713 [terpolymer of vinylcaprolactam, vinylpyrrolidone, and (dimethylamino) ethyl methacrylate] (Cohen et al, 1997).

During experiment, induction time was measured from the beginning of the injection at stabilised condition, and differential pressure across micromodel was recorded. These data were used to indicate initial hydrate formation and duration for total blockage in the micromodel under flow condition. Visual observation on hydrate growth, build-up and deposits were captured through video recording and still pictures.

The blank test was first established by simultaneously injecting presaturated water and natural gas at 11°C subcooling and 109 bar. Based on the differential pressure profile shown in Figure 2.10, it was observed that hydrate started to form after 0.25 hour of induction time. The system pressure was continuously build-up due to injection of fluid until the blockage occurred after passing 7.2 hours of initial hydrate formation. The sequential still pictures are shown in Figure 2.11. As can be seen, a continuous solid and non porous hydrate blocked the capillary tubes.
In the presence of 0.5 mass% PVCap, hydrate did not form at 8°C (11°C subcooling) after leaving the system at this condition for 64 hours. Then, the system temperature was further reduced to 6°C (13°C subcooling). Hydrate formed at this condition with induction time of 1.23 hours as shown by differential pressure profile in Figure 2.12. In this case, total blockage in the capillary tubes occurred after 13.6 hours of initial hydrate formation. As expected, the presence of PVCap would slow down hydrate growth, delay blockage and also prevent hydrate formation in water phase as compared to blank test without inhibitor. As seen in Figure 2.13, hydrate deposits initially appeared to be more porous. As time progressed, more hydrate formed which finally turned to a non porous solid and lead to blockage within capillary tubes.

Another test was carried out in the presence of mixture 0.5 mass% PVCap and 0.75 mass% PGPE. Hydrate did not form at 8°C (11°C subcooling) after 45 hours. The temperature was further reduced to 6°C (13°C subcooling) and left for more than 60 hours. The temperature was further decreased to 4°C (15°C subcooling) and hydrate formed after 1.63 hours induction time. The blockage occurred after passing 23.8 hours of initial hydrate formation. Hydrate formed as a thin deposits and also solid hydrate in several parts of capillary tubes (Figure 2.15).

The summary of results for flow test is given in Table 1. It is interesting to note that in the presence of PGPE as a synergist to PVCap, hydrate formed at higher degree of subcooling with slightly longer induction time and more delay in hydrate blockage as compared to PVCap without synergist. This suggest that PGPE enhances the performance of PVCap base polymer to inhibit hydrate formation and delay hydrate growth. Further tests are proposed to be carried out to study the effect of various synergist concentration and other factors such as injection rate, pressure and water oil ratio on hydrate deposits within micromodel.
Figure 2.10. Differential pressure profile for Natural Gas – Water system at 109 bar. Hydrate formed at 8°C (11°C subcooling).

(a) 3 hrs after formation, \( \Delta P = 12 \) bar
(b) 8 hrs after formation, \( \Delta P = 26 \) bar
(c) 24 hrs after formation, \( \Delta P = 27 \) bar

Figure 2.11. Images of hydrate deposits for Natural Gas – Water system at 109 bar, 8°C (11°C subcooling).
Figure 2.12. Differential pressure profile for Natural Gas – Water system with 0.5 mass% PVCap at 109 bar. Hydrate formed at 6°C (13°C subcooling)

(a) 0.8 hrs after formation, \( \Delta P = 3 \) bar  
(b) 4 hrs after formation, \( \Delta P = 10 \) bar  
(c) 10 hrs after formation, \( \Delta P = 32 \) bar

Figure 2.13. Images of hydrate deposits for Natural Gas – Water system with 0.5 mass% PVCap at 109 bar, 6°C (13°C subcooling).
Figure 2.14. Differential pressure for Natural Gas – Water system with 0.5 mass% PVCap + 0.75 mass% PGPE at 109 bar. Hydrate formed at 4°C (15°C subcooling)

(a) 0.3 hrs after formation, $\Delta P = 2$ bar
(b) 2 hrs after formation, $\Delta P = 10$ bar
(c) 24 hrs after formation, $\Delta P = 49$ bar

Figure 2.15. Images of hydrate deposits for Natural Gas – Water system with 0.5 mass% PVCap + 0.75 mass% PGPE at 109 bar, 4°C (15°C subcooling)

Table 1: Results of flow test by HP Micromodel
Chapter 2 Micromodel Experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hydrate formation temperature (°C)</th>
<th>Subcooling (°C)</th>
<th>Induction time at subcooling (hr)</th>
<th>Time for blockage (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>8</td>
<td>11</td>
<td>0.25</td>
<td>7.2</td>
</tr>
<tr>
<td>0.5 mass% PVCap</td>
<td>6</td>
<td>13</td>
<td>1.23</td>
<td>13.6</td>
</tr>
<tr>
<td>0.5 mass% PVCap + 0.75 mass% PGPE</td>
<td>4</td>
<td>15</td>
<td>1.63</td>
<td>23.8</td>
</tr>
</tbody>
</table>

2.4. SUMMARY OF RESULTS

The experiments for natural gas-water system with 5 volume% of a new kinetic inhibitor (labelled as HT04-049) were carried out in high pressure micromodel set-up to study the mechanism of hydrate formation and crystal morphology in comparison with those of Luvicap® (1 mass% PVCAP).

The result at 105 bar and 16 °C subcooling showed that hydrate formation began at the interface of gas and water followed by a slow growth of small hydrate particles within the gas bubbles, which finally covered the whole gas bubbles profile. The hydrate particles turned into transparent and thin patches of crystals. In the experiment carried out at 95 bar, hydrate formed at 13.7°C subcooling in the outlet tubing of micromodel. Hydrate crystals turned into transparent thin patches of crystal similar to that at 105 bar. Hydrate formation was further induced by reducing the temperature to 2.6°C (15.4°C subcooling). The mechanism of initial hydrate formation and morphology was similar to that observed at earlier condition.

Hydrate morphology and crystal growth between HT04-049 and Luvicap® was compared. The results showed that the crystal morphology are significantly different. In the presence of HT04-049 a thin patches of hydrate crystals formed which was similar to that in the presence of HI03-24 reported in the previous JIP meeting. The result also suggested that 5 vol% HT04-049 is less effective than Luvicap® in delaying hydrate crystal growth.

Characteristic behaviour of hydrate plugging with and without LDHI and/or synergist at simulated pipeline conditions was investigated under flowing condition. The results showed that PGPE enhances the performance of PVCap base polymer to inhibit
hydrate formation and delay hydrate growth. In the presence of PGPE as a synergist to PVCap, hydrate formed at higher degree of subcooling with slightly longer induction time and further delay in hydrate blockage as compared to PVCap without synergist and also the blank test.

The morphology for blank test at 11°C subcooling was in the form of a continuous non-porous solid hydrate, while in the presence of 0.5 mass% PVCap at 13°C subcooling, hydrate deposits initially appeared to be more porous and progressively turned to a non porous solid. In the presence of mixture 0.5 mass% PVCap and 0.75 mass% PGPE at 15°C subcooling, hydrate initially formed as a thin deposits and also solid hydrate in several parts of capillary tubes. Continuous flow of water and gas into the capillary tubes lead to buildup of solid hydrate and finally blocked the capillatry tubes.

2.5. Reference

CHAPTER 3
KINETICS RIG EXPERIMENTS

3.1. INTRODUCTION
In the previous period of project, the performance of three new formulations of PVCap based kinetic inhibitors, containing different synergist chemical was studied in various conditions. In the past six months, the study extended to investigation on the performance of a new base polymer, and the effect of a known synergist chemical and a commercial corrosion inhibitor on the performance of PVCap. Three series of experiments were conducted using the kinetic rig. The first was to test a new base polymer in order to find out the range of its applicability in different conditions. The performance of the inhibitor in terms of induction time was tested in different degrees of subcooling in natural gas-water system. The inhibitor was also assessed in two hydrodynamic conditions; shut-in and flowing (stirring) conditions. The second series of tests were carried out on a synergist chemical with PVCap in natural gas system in the kinetic rig at static and mixing conditions and at different degrees of subcooling. Finally, the impact of a commercial corrosion inhibitor on the performance of PVCap was evaluated in a kinetic rig at various conditions.

3.2. TESTING A NEW BASE POLYMER HYTREAT 04-049
The new KHI (labelled as HYTREAT® 04-049) was supplied by Clariant Oil Services, which is composed of the BASF new advanced polymer, water and a solvent. The performance of the kinetic inhibitor was assessed in terms of induction time in natural gas-water system, by conducting experiments in a kinetic rig. In all the tests as suggested (by Clariant Oil Services) a concentration of 5 volume% of the inhibitor in deionised water was used. The details of the tests and results are presented below.

3.2.1. NATURAL GAS-WATER SYSTEM
A total of sixteen experiments were carried out using Kinetic Rig 1 to measure the induction times in a natural gas-water system with 5 vol% of HYTREAT® 04-049 at different conditions. The composition of the natural gas (LAB-NG) used in the tests has been shown in Table 3.1. The hydrate phase boundary for the system was predicted by the in-house hydrate software (HWHYD) (Figure 3.1) and used for the
calculation of degree of subcooling at the testing conditions. The experimental results are summarised in Table 3.2 and the corresponding pressure and temperature profiles measured in the experiments are presented in Appendix B (Figures 1-16).

### Table 3.1. Composition of the natural gas (LAB-NG) used in the experiments

<table>
<thead>
<tr>
<th>Component</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>i-C₄</th>
<th>n-C₄</th>
<th>i-C₅</th>
<th>n-C₅⁺</th>
<th>N₂</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol%</td>
<td>89.0</td>
<td>5.50</td>
<td>1.50</td>
<td>0.16</td>
<td>0.31</td>
<td>0.07</td>
<td>0.11</td>
<td>1.70</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Figure 3.1. Natural gas-water hydrate phase boundary predicted using the in-house model.

The first two tests were carried out at 4.3 °C and 100 bar corresponding to 14.2 °C subcooling (Table 3.2 Tests No. 1-2) and 4-5 hours induction time was observed. By increasing the temperature and reducing the subcooling stepwise to 13.2 °C (Tests No.3-6), the induction times were no longer than 7 hours. In the subsequent experiments at degrees of subcooling lower than 11.2 °C, induction times longer than one day were achieved by the inhibitor at mixing conditions (Tests No.10-11). It is worth to notice the changes of induction times in the range of 11-12.5 °C and 14.2-13.2 °C subcooling.
At static (shut-in) conditions, the induction times are similar to those of mixing conditions at similar degrees of subcooling (Table 3.2), and as expected, the rate of hydrate growth is much lower than those of mixing conditions tests (Figure 3.2). This trend is on the contrary to that of HI03-24 kinetic inhibitor where at static conditions the rate of hydrate growth was much more than that of mixing condition tests (Figure 3.3, taken from previous progress report for comparison).

Table 3.2. Experimental results obtained from the kinetics rig for 5vol% kinetic inhibitor (HYTREAT04-049) solution in the presence of natural gas.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P °C / bar</th>
<th>Subcooling / °C</th>
<th>Induction time / hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>4.3 / 100</td>
<td>14.2</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>4.3 / 100</td>
<td>14.2</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>4.9 / 100</td>
<td>13.6</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>4.9 / 100</td>
<td>13.6</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>600</td>
<td>5.3 / 100</td>
<td>13.2</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>600</td>
<td>5.3 / 100</td>
<td>13.2</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>600</td>
<td>6.0 / 100</td>
<td>12.5</td>
<td>11</td>
</tr>
<tr>
<td>8</td>
<td>600</td>
<td>6.7 / 101</td>
<td>11.9</td>
<td>12</td>
</tr>
<tr>
<td>9</td>
<td>600</td>
<td>7.4 / 101.4</td>
<td>11.2</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>7.5 / 101.5</td>
<td>11.1</td>
<td>48</td>
</tr>
<tr>
<td>11</td>
<td>600</td>
<td>7.6 / 101.4</td>
<td>11</td>
<td>30</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>4.3 / 100</td>
<td>14.2</td>
<td>4</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>4.9 / 100</td>
<td>13.6</td>
<td>4</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>7.1 / 101</td>
<td>11.5</td>
<td>6</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>7.3 / 101</td>
<td>11.3</td>
<td>7</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>7.3 / 101</td>
<td>11.3</td>
<td>13</td>
</tr>
</tbody>
</table>
Figure 3.2. Pressure profiles of the tests (No. 4, 9, 13 and 16) in natural gas-water system in the presence of 5vol% kinetic inhibitor (HYTREAT® 04-049) in the kinetic rig in mixing and, static conditions.

Figure 3.3. Pressure profiles of the tests in natural gas-water system in the presence of 5vol% kinetic inhibitor (HI03-24) in the kinetic rig in mixing (600rpm) and, static conditions.
3.3. THE EFFECT OF SYNERGIST CHEMICAL ON THE PERFORMANCE OF KINETIC INHIBITOR (PVCAP)

A comprehensive study on a known synergist chemical for a kinetic inhibitor (PVCap) was suggested in the previous steering committee meeting. The information about synergist chemicals for kinetic inhibitors is very limited in the open literature. Cohen and co-workers (Cohen J.M., Wolf P.F., and Young W.D., 1998) have reported that adding a small amount of glycol ether (2-butoxyethanol, for example) substantially improves the performance of the PVCap and VC-713 [terpolymer of vinylcaprolactam, vinylpyrrolidone, and (dimethylamino) ethyl methacrylate]. Their experimental results have showed that 2-butoxyethanol (Ethylene glycol monobutyl ether) appeared to be better synergist than other glycol ethers tested. However because it is a toxic chemical, 1-propoxy-2-propanol (Propylene glycol propyl ether), hereafter PGPE, which is not toxic, was used as synergist in this study.

A series of tests conducted in Kinetic rig 1, on natural gas-water water system in the presence of 0.5 mass% PVCap and different concentrations of PGPE as synergist. The results of the tests have been summarised in Table 3.3, and the pressure and temperature profiles of the tests are presented in the Appendix B (Figures 17-27). As presented in Table 3.3, at 14 °C subcooling, addition of 0.5mass% and 0.75 mass% of synergist to the system of natural gas-water-0.5mass% PVCap have increased the induction time by 7 and 11 hours respectively (Tests No1-4).

Table 3.3. Experimental results obtained from the kinetics rig 1 for 0.5 mass% PVCap and different concentration of PGPE as synergist in the presence of natural gas at 600 rpm.

<table>
<thead>
<tr>
<th>Test No</th>
<th>Synergist mass%</th>
<th>Testing T/P °C / bar</th>
<th>Subcooling °C</th>
<th>Induction Time/hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>4.5 / 100</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>4.4 / 100</td>
<td>14.1</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>4.4 / 98</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>4.3 / 98</td>
<td>14.1</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>4.6 / 100</td>
<td>13.9</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>4.6 / 100</td>
<td>13.9</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>0.75</td>
<td>4.5 / 98</td>
<td>13.9</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>0.75</td>
<td>4.8 / 100</td>
<td>13.7</td>
<td>27</td>
</tr>
<tr>
<td>9</td>
<td>0.75</td>
<td>4.8 / 100</td>
<td>13.7</td>
<td>27</td>
</tr>
<tr>
<td>10</td>
<td>0.75</td>
<td>4.9 / 100</td>
<td>13.6</td>
<td>32</td>
</tr>
<tr>
<td>11</td>
<td>0.75</td>
<td>4.9 / 100</td>
<td>13.6</td>
<td>30</td>
</tr>
</tbody>
</table>

3.5
Again at 13.9 °C subcooling, 0.75 mass% of PGPE showed better synergism effect than that of 0.5mass% (Tests No. 5-7). Figure 3.4 illustrates the pressure profiles and induction times of the above tests. From the results of the tests, it seems that in the range of subcooling tested, PGPE has a synergistic effect on PVCap performance. In the presence of 0.75 mass% PGPE, by decreasing the degree of subcooling to 13.6 °C, the induction time extended to 30 hours. In the presence of synergist, good repeatability of the tests was observed (Tests No.8-11).

The higher concentration of PGPE (0.75 mass%) was selected and used for the further study of the system in the visual kinetic rig, High Pressure Micromodel set-up, and Ultrasonic rig. The results of those tests have been presented in the related chapters of this report.

![Figure 3.4](image.png)

Figure 3.4. Comparison of pressure profiles / induction times of the tests in natural gas-water system in the presence of 0.5mass% PVCap and different concentration of synergist in the presence of natural gas and water, at 600rpm.

The synergistic effect of PGPE on PVCap was evaluated at static conditions at 14.1°C subcooling by conducting four experiments in the kinetic rig. The temperature and pressure profiles of the tests have been shown in the Appendix B (Figures 28-31). The pressure profiles of the tests have been compared in Figure 3.5. As seen in the Figure 3.5, PGPE has decreased the rate of growth at static conditions at 13.5-14.1 °C subcooling.
Figure 3.5. Comparison of pressure profiles / induction times of the tests in natural gas-water system in the presence of 0.5mass% PVCap and 0.75mass% PGPE in the presence of natural gas and water at static conditions.

3.4 THE EFFECT OF CORROSION INHIBITOR ON KINETIC INHIBITOR

In last steering committee meeting, it was suggested to study the effect of corrosion inhibitors on the performance of the kinetic inhibitors. In this study the effect of a commercial corrosion inhibitor (labelled as Corrtreat 799, and provided by Clariant Oil Services) on the performance of LUVICAP® (40 mass% PVCap and 60 mass% ethylene glycol), in terms of induction time was investigated.

A total of eleven experiments carried out in a kinetic rig in different testing conditions in the presence of natural gas-water and mixture of above mentioned inhibitors. In the tests a solution of 1 mass% PVCap and 500 ppm (as suggested by Clariant Oil Services) of above corrosion inhibitor in water was used. The summary of the tests is presented in Table 3.4 and the pressure and temperature profiles of the tests are presented in the Appendix B (Figures 32-42).
Table 3.4. Experimental results obtained from the kinetic rig for solution of 1mass% PVCap and 500 ppm Corrtrate 799 in water in the presence of natural gas.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P (°C / bar)</th>
<th>Subcooling (°C)</th>
<th>Induction (Time / hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>4.4 / 70.5</td>
<td>12.1</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>5.0 / 72</td>
<td>11.5</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>5.3 / 71</td>
<td>11.2</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>5.3 / 73</td>
<td>11.3</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
<td>6.0 / 71.5</td>
<td>10.5</td>
<td>&gt;36</td>
</tr>
<tr>
<td>6</td>
<td>1000</td>
<td>5.9 / 70</td>
<td>10.6</td>
<td>&gt;36</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>5.2 / 71</td>
<td>11.2</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>5.2 / 71</td>
<td>11.2</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>6.3 / 71</td>
<td>10.1</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>6.2 / 71</td>
<td>10.2</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>7.0 / 70.7</td>
<td>9.4</td>
<td>&gt;36</td>
</tr>
</tbody>
</table>

As shown in Table 3.4, the tests conducted in pressure range of 70-73 bar. In the range of 12.1-11.2 °C subcooling, 2-7 hours induction time was observed (Tests No. 1-3). Only at degrees of subcooling less than 11 °C, induction times longer than one day achieved by the hydrate inhibitor. Five experiments carried out on the above system at static conditions (Tests No.7-11). At 11.2 °C subcooling similar induction times as those in mixing conditions were observed (Compare with Tests No.3-4). However at lower degrees of subcooling shorter induction times was achieved by kinetic inhibitor than those of tests with mixing (Tests No.10-11).

For comparison, two experiments conducted in the absence of corrosion inhibitor on natural gas-water-1mass% PVCap and similar conditions of above tests. The pressure and temperature profiles of the tests are presented in the Appendix B (Figures 43-44). At 11.6-11.8 °C subcooling the induction times found to be longer than one day. Comparing the above results with those of tests in the presence of corrosion inhibitor (Tests No.3-4 of Table 3.4) shows that corrosion inhibitor has a negative impact on the performance of PVCap. It should be noticed that in the subcooling range (9.4-12.1°C) the experiments carried out in the presence of corrosion inhibitor the pressure drop recorded was not mainly less than 10 bar.

3.5. SUMMARY AND DISCUSSIONS

The BASF advanced polymer, was tested in natural gas-water system at various conditions. From the results of the tests on 5vol% of the new base polymer it appeared that for achieving the induction times longer than one day, the degree of subcooling should be less than 11.2 °C for natural gas system. At static conditions and same...
temperatures and pressures of those tests with mixing, similar induction times and lower rates of hydrate growth were observed.

As a part of comprehensive study on a known synergist chemical for PVCap, propylene glycol propyl ether was selected and its synergistic effect on PVCap performance, at two different concentrations, was tested in the presence of natural gas-water system at different conditions. The results of the experiments at the range of degrees of subcooling tested (13.9-14.1 °C), showed the PGPE synergistic effect on the PVCap performance. Increasing the concentration of PGPE from 0.5 to 0.75 mass% improved its synergistic effect. It also improved PVCap performance in hydrate inhibition at static conditions by decreasing the rate of hydrate growth.

The effect of a commercial corrosion inhibitor (Corrware 799 provided by Clariant Oil Services) on the performance of PVCap was studied by conducting a series of tests in the system of natural gas-water-1 mass% PVCap in the presence and absence of corrosion inhibitor at different conditions. The tests results showed that in the presence of corrosion inhibitor, and 1 mass% PVCap, induction times longer than 1 day is achievable at degrees of subcooling less than 11°C. Considering the fact that in the absence of corrosion inhibitor similar induction times were achieved at 11.8°C subcooling, it appeared that corrosion inhibitor tested has a negative impact on the performance of PVCap. At static conditions, in the presence of corrosion inhibitor, again shorter induction times were observed at similar conditions of those tests in the absence of corrosion inhibitor.

**REFERENCE**
CHAPTER 4
HIGH PRESSURE VISUAL RIG EXPERIMENTS

4.1. INTRODUCTION

During the course of this research project tests have been conducted in a high pressure visual rig in order to observe the growth pattern of hydrates in static conditions. The reason for this is to compliment work conducted in the kinetic rigs, the micromodel and the ultrasonic rig. The visual observations can for example be used to support and possibly explain test results from other rigs. In addition the observations may in themselves yield valuable information.

During the last six months tests have been concentrated on three areas. Firstly the effect of ethylene glycol on the growth pattern of natural gas and methane hydrates. Previous tests had shown that unusual hydrate growth patterns were observed when LUVICAP® was present. LUVICAP® is composed of a polymer and ethylene glycol and hence it was necessary to find the effect of ethylene glycol on its own. An additional test was conducted to find the effect of methanol on the growth pattern of hydrates formed from natural gas. The second area of work was to study the growth pattern seen for natural gas and methane hydrates in the presence of a new inhibitor, HYTREAT® 04-049, which was being tested in the other experimental rigs. The third area of work was to study the effect of a synergic component, propylene glycol propyl ether (PGPE), on the growth pattern of natural gas hydrates in the presence of HYTREAT® 04-049 and in a separate test LUVICAP®. These tests were again conducted to compliment work on other rigs.

The high pressure visual rig can also be used to measure interfacial tension (IFT) using the pendant drop technique. Measurements are in progress to investigate the effect of the hydrate inhibitor, HYTREAT® 04-049, on IFT. It is planned to present the results of this study at the project steering committee meeting in December.
4.2. EXPERIMENTAL EQUIPMENT AND METHODS
The experimental set-up is comprised of a high pressure cylinder fitted with sapphire windows at both ends. The cell can be used at pressures up to 517 bar and at temperatures between −30 and +50°C. The cell temperature is controlled by circulating water from a heater/chiller through an inbuilt jacket. A platinum resistance temperature probe monitors the cell temperature. The pressure of the cell is monitored by a strain gauge pressure transducer connected to the cell via a high pressure line. The accuracy of the temperature measurement is ±0.1°C and the pressure ±0.3 bar. A computer is used to log the cell pressure and temperature. A schematic of the experimental rig is shown in Figure 4.1. The cell is mounted on a rocking mechanism in order to give mixing when required.

![Schematic of high pressure (517bar) visual cell.](image)

Figure-4.1. Schematic of high pressure (517bar) visual cell.
For the tests reported here 50cc of liquid was injected into the cell and then gas was injected to the desired start point pressure. The cell was mixed to equilibrate the contents and then held in a horizontal position in order to make visual observations with the aid of a magnifying camera.

Distilled water was used in all tests. The ethylene glycol was 99.5% pure and the methanol was 99+% pure. The methane was 99.995% pure. The composition of the natural gas is given in Table 4.1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>3.24</td>
</tr>
<tr>
<td>C₁</td>
<td>87.32</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.36</td>
</tr>
<tr>
<td>C₂</td>
<td>5.67</td>
</tr>
<tr>
<td>C₃</td>
<td>1.68</td>
</tr>
<tr>
<td>iC₄</td>
<td>0.23</td>
</tr>
<tr>
<td>nC₄</td>
<td>0.40</td>
</tr>
<tr>
<td>iC₅</td>
<td>0.10</td>
</tr>
</tbody>
</table>

4.3. EXPERIMENTAL RESULTS AND OBSERVATIONS-GROWTH PATTERN WITH ETHYLENE GLYCOL AND WITH METHANOL

4.3.1. Natural gas with an aqueous solution of ethylene glycol

The cell was loaded with an aqueous solution composed of 1.5 mass% ethylene glycol and natural gas. The cell was cooled from 35°C to 4°C over 12 hours. At 4°C and the cell pressure of 106 bar the system was around 14.5°C below the hydrate phase boundary. The cell pressure and temperature were recorded and visual observations of hydrate formation made. The pressure and time data are shown in Figure 4.2 along with the data from previous tests with distilled water and with an aqueous solution composed of 2.5 mass% LUVICAP®. Figure 4.2 shows that there are significant differences in the pressure/time data for the three tests. As discussed in previous reports the distilled water data shows only a slow pressure drop over time whereas in the test with LUVICAP® the pressure dropped quite rapidly soon after the cell temperature had cooled to 4°C. The new data for hydrate formation with an aqueous
solution of ethylene glycol showed a stable pressure for around 4.5 hours after the cell temperature had cooled to 4ºC and then a very rapid pressure drop over around 0.3 hours followed by a continuous but slower pressure drop with time.

![Diagram showing pressure and time data for tests with natural gas in the presence of distilled water, natural gas in the presence of 1.5 mass% ethylene glycol, and natural gas in the presence of 2.5 mass% LUVICAP®.](image)

Figure-4.2. Pressure and time data for tests with natural gas in the presence of distilled water, natural gas in the presence of 1.5 mass% ethylene glycol, and natural gas in the presence of 2.5 mass% LUVICAP®.

Visual observations from previous work were that in the test with distilled water hydrates formed mainly at the gas/water interface with only a few needle-like crystals growing down into the water from the interface. In the case of the test with LUVICAP® hydrate growth began at the gas/water interface and then spread up the internal walls of the cell appearing to pull the water from the lower to upper part of the cell eventually removing all of the water. Hydrate formation then continued with the accompanying pressure reduction. In the test with ethylene glycol no hydrate formation was seen until 4.5 hours after the cell temperature had cooled to 4ºC. This induction time was found to be variable in repeats of the test, in one case it was over 10 hours. Once hydrate formation occurred it was rapid, starting at the gas water interface and spreading up the internal walls of the cell. As with the LUVICAP® test the water appeared to be pulled up the cell. In this case though gas bubbles came in behind the original gas/water interface, where the hydrate growth started, and hydrates...
formed rapidly across their surface. During this period the pressure reduced rapidly. Hydrate formation then continued indicated by a declining pressure and a bulking up of the mass of hydrates present in the cell visualised by a darkening of the hydrate mass.

Figures 4.3 through 4.7 show still images from the film captured of the hydrate formation. Figures 4.3 through 4.6 show hydrate formation starting at the gas/water interface and then continuing up the internal surface of the sapphire window whilst gas bubbles appear below the growing hydrate layer. Hydrate formation can be seen at the surface of the gas bubbles in Figures 4.6 and 4.7.

Figure-4.3. Picture showing natural gas hydrate formation starting at the gas/water (1.5 mass% ethylene glycol) interface. The temperature probe can be seen in the centre at the bottom of the picture.
Figure-4.4. Picture showing natural gas hydrate formation starting at the gas/water (1.5 mass% ethylene glycol) interface and continuing up the sapphire window. A bubble of gas is seen below the interface.

Figure-4.5. Picture showing natural gas hydrate formation starting at the gas/water (1.5 mass% ethylene glycol) interface and continuing up the sapphire window. The gas bubble is seen to increase in size.
Figure-4.6. Picture showing natural gas hydrate formation starting at the gas/water (1.5 mass% ethylene glycol) interface and continuing up the sapphire window. Hydrates can be seen forming on the surface of the bubble.

Figure-4.7. Picture showing natural gas hydrate formation on the surface of gas bubbles in the liquid phase.
4.3.2 Methane with an aqueous solution of ethylene glycol

The same test procedure was used as that for the natural gas test but with methane and a higher start pressure and in addition the cell temperature was cooled from 35°C to 4°C over a period of 19 hours. At 4°C and the cell pressure of 117 bar the system was around 9°C below the hydrate phase boundary. The pressure and time data are presented in Figure 4.8 along with previously recorded data from tests with methane and distilled water and methane and an aqueous solution of LUVICAP®. In the previous tests the temperature was cooled over 12 hours so there is a difference in the pressure profile for the cooling stage of the tests compared with the new data with ethylene glycol. This would not be expected to influence the outcome of the test, which is quite clear. The tests with distilled water and with 1.5 mass% ethylene glycol show similar patterns in that there was only a slow pressure reduction over time. In contrast the test with LUVICAP® showed a pressure drop around 40 hours after the start of the test.

Figure 4.8. Pressure and time data for tests with methane in the presence of distilled water, methane in the presence of 1.5 mass% ethylene glycol, and methane in the presence of 2.5 mass% LUVICAP®.

Visual observations from previous tests with methane with distilled water were that in the case of methane with distilled water, gas hydrates only formed at the gas/water interface with a few needle like crystals growing into the water from the interface. In contrast in the test
with LUVICAP®, hydrates had started forming at the gas/water interface and then continued in all parts of the cell. The growth pattern was not the same as that with natural gas and LUVICAP® where the hydrates formed mainly in the upper part of the pressure vessel. Figures 4.9 through 4.13 show the growth pattern of the methane hydrates in the presence of an aqueous solution composed of 1.5 mass% ethylene glycol. As can be seen the hydrates form a layer at the gas/water interface and then there is a small amount of hydrate formation into both the gas and liquid phases from the interface. However the amount of hydrates formed is small both visually and in terms of pressure reduction.

Figure-4.9. The gas/water interface in the test with methane and an aqueous solution of ethylene glycol prior to hydrate formation.
Figure-4.10. Hydrate formation at the gas/water interface in the test with methane and an aqueous solution of ethylene glycol.

Figure-4.11. Hydrate formation at the gas/water interface in the test with methane and an aqueous solution of ethylene glycol, hydrate beginning to grow into the liquid and gas phases.
Figure-4.12. Hydrate formation at the gas/water interface in the test with methane and an aqueous solution of ethylene glycol, hydrate continuing to grow into the liquid and gas phases.

Figure-4.13. Hydrate formation at the gas/water interface in the test with methane and an aqueous solution of ethylene glycol, hydrate continuing to grow into the liquid and gas phases.
4.3.3. **Natural gas with an aqueous solution of methanol**

One further test was conducted to see the effect of a different inhibitor on the pattern of hydrate growth. In this test an aqueous solution composed of 1.5 mass% methanol was used and the temperature was reduced to 4°C over a period of 19 hours. The pressure and time data are shown in Figure 4.14 along with the data for the test with ethylene glycol. As can be seen from Figure 4.14 the pressure time data show similar patterns in that there is an induction time with no pressure reduction followed by a rapid period of pressure reduction/hydrate formation and this is followed by a steady pressure reduction. In the test with methanol the rate of pressure reduction after the initial rapid drop is slower than that for the test with ethylene glycol.

![Figure 4.14. Pressure and time data for tests with natural gas in the presence of 1.5 mass% ethylene glycol, and natural gas in the presence of 1.5 mass% methanol.](image-url)

The growth pattern of the natural gas hydrates in the presence of an aqueous solution composed of 1.5 mass% methanol was similar to that seen in the test with ethylene glycol. Formation started at the gas/water interface and hydrates formed on the internal surfaces of the cell in the vapour phase. No film was obtained of bubbles forming below the hydrate layer as the formation occurred at night and the camera was not moved however visual observations of the hydrate mass at a later time indicated that this had occurred. Figures 4.15 through 4.17 show the start of hydrate formation.
Figure-4.15. The start of natural gas hydrate formation at the gas/water interface in the test with natural gas and an aqueous solution of methanol.

Figure-4.16. Natural gas hydrate formation at the gas/water interface and on the cell window in the test with natural gas and an aqueous solution of methanol.
Figure-4.17. Natural gas hydrate formation at the gas/water interface and on the cell window in the test with natural gas and an aqueous solution of methanol.

4.4. EXPERIMENTAL RESULTS AND OBSERVATIONS-GROWTH PATTERN WITH HYTREAT® 04-049 WITH NATURAL GAS AND WITH METHANE

4.4.1. Natural gas with HYTREAT® 04-049

In both tests (natural gas and methane) with HYTREAT® 04-049, which is composed of the BASF new advanced polymer, water and a solvent, an aqueous solution made up from 5 volume% inhibitor and 95 volume% distilled water was used. In the test with natural gas the temperature was reduced from 35°C to 4°C over 21 hours. The pressure and time data for the test with natural gas is shown in Figure 4.18 and as can be seen hydrate formation, indicated by a rapid reduction in pressure occurred when the cell temperature reached 4°C. There was no induction time and the conversion of the liquid to hydrates was rapid and efficient. The pattern of growth was similar to that seen in the tests with LUVICAP® in that hydrate formation took place mainly in the upper part of the cell appearing to pull the water with it.
Figure-4.18. Pressure and time data for test with natural gas in the presence of 5 volume% HYTREAT® 04-049.

Figures 4.19 through 4.22 show stills from the film of the hydrate growth phase. In Figures 4.19 and 4.20 the start of hydrate formation can be seen on the sapphire window. A large number of hydrate particles were seen in the liquid phase, mainly moving towards the gas/water interface. It is clear from these pictures that a solid layer of hydrates did not form at the interface as had been seen in the tests with natural gas/aqueous solution of ethylene glycol and natural gas/aqueous solution of methanol. Figure 4.21 shows hydrates forming in the top part of the cell growing downwards. Figure-4.22 shows hydrates forming in the upper part of the cell and “channels” of water moving up the cell. In this picture hydrate that had fallen from the upper part of the cell can be seen floating at the gas/water interface, once in the water interface the hydrate crystals did not grow further.
Figure-4.19. Natural gas hydrate formation at the gas/water interface and on the cell window in the test with natural gas and an aqueous solution of HYTREAT® 04-049.

Figure-4.20. Natural gas hydrate formation at the gas/water interface and on the cell window in the test with natural gas and an aqueous solution of HYTREAT® 04-049.
Figure-4.21. Natural gas hydrate formation in the upper part of the high pressure cell in the test with natural gas and an aqueous solution of HYTREAT® 04-049.

Figure-4.22. Natural gas hydrate formation in the test with natural gas and an aqueous solution of HYTREAT® 04-049. Hydrates can be seen forming on the sapphire window and water appears to be drawn upwards in channels. A solid layer of hydrate is not seen at the interface.
4.4.2. Methane with HYTREAT® 04-049

In this test the temperature was lowered from 35°C to 4°C over 19 hours, the pressure and time data are shown in Figure 4.23 below. It can be seen from Figure 4.23 that there was an induction time of around 8 hours after the cell temperature had reached 4°C prior to a sharp pressure reduction indicating hydrate formation. This sharp pressure reduction was followed by a slow pressure reduction with time. In terms of the pressure/time “profile” the pattern was similar to that seen in the test with methane with an aqueous solution of methanol, however in the methanol test the pressure reduction during the rapid hydrate formation stage was greater.

![Figure 4.23. Pressure and time data for tests with methane in the presence an aqueous solution of HYTREAT® 04-049.](image)

The growth pattern seen during the rapid pressure drop phase was similar to that seen in the test with natural gas and HYTREAT® 04-049. Figures 4.24 through 4.26 show the stills from the recorded images of the hydrate growth. Figures 4.24 and 4.25 show the start of hydrate formation and as can be seen these are similar to Figures 4.19 and 4.20 from the natural gas test. The pressure reduction began to slow as the bulk of hydrates in the upper part of the cell grew rapidly, becoming denser as seen in Figure-4.26. As with the natural gas/HYTREAT® 04-049 test the gas/water interface is not covered by a continuous layer of hydrates during the rapid growth stage.
Figure-4.24. Methane hydrate formation at the gas/water interface and on the cell window in the test with methane and an aqueous solution of HYTREAT® 04-049.

Figure-4.25. Methane hydrate formation at the gas/water interface and on the cell window in the test with methane and an aqueous solution of HYTREAT® 04-049.
Figure-4.26. Methane hydrate formation on the cell window in the test with methane and an aqueous solution of HYTREAT® 04-049. The bulk of hydrates in the upper part of the cell can be seen increasing.

4.5. EXPERIMENTAL RESULTS AND OBSERVATIONS-GROWTH PATTERN OF NATURAL GAS HYDRATES WITH PGPE ADDED TO HYTREAT® 04-049 AND PGPE ADDED TO LUVICAP®

4.5.1. Natural gas with an aqueous solution of PGPE and HYTREAT® 04-049

In this test an aqueous solution comprised of 5 volume% HYTREAT® 04-049 and 1.7 volume% PGPE was used. The pressure and time data for this test and the test with 5 volume% HYTREAT® 04-049 are compared in Figure-4.27 below. As can be seen from Figure 4.27 in the test with PGPE there is a small induction time followed by a rapid pressure reduction followed by slow pressure reduction with time. This contrasts with the test with no PGPE where the pressure reduction was much greater after which the pressure did not decline significantly with time.
Figure 4.27. Pressure and time data for tests with natural gas in the presence of aqueous solutions of HYTREAT® 04-049/PGPE and HYTREAT® 04-049.

The two tests without and with PGPE from a visual point of view showed similar growth patterns. Figures 4.28 through 4.30 show stills from the captured images for the test with HYTREAT®04-049/PGPE. Initial hydrate formation started at the gas/liquid interface and continued in the upper part of the cell as shown in Figures 4.28 and 4.29. All of the water was removed from the lower part of the cell as shown in Figure 4.30. This phase of hydrate formation occurred during the initial rapid pressure decline. Hydrate formation continued as seen by a pressure decline and a darkening of the hydrate mass.
Figure-4.28. Hydrate formation starting at the gas/water interface in the test with natural gas and an aqueous solution of HYTREAT® 04-049/PGPE.

Figure-4.29. Hydrate formation in the upper part of the cell gas/water in the test with natural gas and an aqueous solution of HYTREAT® 04-049/PGPE.
Figure 4.30. Hydrate formation in the test with natural gas and an aqueous solution of HYTREAT® 04-049/PGPE. All of the water has been removed from the lower part of the cell.

4.5.2. Natural gas with an aqueous solution of LUVICAP® and PGPE

An aqueous solution comprised of 1.25 mass% LUVICAP® and 0.75 mass% PGPE was used in the test. The cell was cooled from 35°C to 4°C over a period of 22 hours. The pressure and time data are plotted in Figure 4.31 and as can be seen there was an induction time of around 5 hours prior to hydrate formation. When hydrate formation occurred the pressure decline was rapid but slowed quickly. In earlier tests with a 2.5 mass% LUVICAP® solution the pressure drop on hydrate formation was greater and more rapid, in addition there was no induction time.
Figure-4.31. Pressure and time data for tests with natural gas in the presence of an aqueous solution of LUVICAP®/PGPE.

Figures 4.32 through 4.34 show images captured during the formation of hydrates in the test with natural gas and LUVICAP®/PGPE. Hydrates were seen to form first at the gas/liquid interface as shown in Figure 4.32. Hydrate formation then continued up from the interface as shown in Figure 4.33. As can be seen from these two figures a layer of hydrates formed at the gas water interface. As the water was drawn from the lower part of the cell gas bubbles appeared below the gas/liquid interface in a similar manner to that seen in the tests with natural gas and an aqueous solution of ethylene glycol as shown in Figures 4.4 through 4.7. The gas bubble became “coated” with a layer of hydrates as shown in Figure 4.34.
Figure 4.32. Hydrate formation at the gas/liquid interface in the test with natural gas and an aqueous solution of LUVICAP®/PGPE.

Figure 4.33. Hydrate formation at the gas/liquid interface and in the upper part of the cell in the test with natural gas and an aqueous solution of LUVICAP®/PGPE.
Figure-4.34. Hydrate formation at the gas/liquid interface, in the upper part of the cell and on the surface of gas bubbles below the interface in the test with natural gas and an aqueous solution of LUVICAP®/PGPE.

4.6. DISCUSSION

The results from the tests investigating the effect of ethylene glycol on the growth pattern of hydrates in a static cell showed that in the case of natural gas there was a significant effect. This was ascertained by comparing tests at the same degree of subcooling (14.5°C) with a system comprised of natural gas and distilled water and a system comprised of natural gas and an aqueous solution comprised of 1.5 mass% ethylene glycol. With distilled water there was only a small amount of hydrate growth at the gas/water interface whereas with the addition of the ethylene glycol there was significant hydrate growth throughout the cell. The ethylene glycol appeared to prevent the formation of a solid hydrate layer capable of halting the flow of water to hydrates growing in the upper part of the cell. A similar effect was seen in a test with an aqueous solution of methanol (1.5 mass%) with natural gas. The growth pattern seen in earlier tests with natural gas and LUVICAP® was not the same as the test with ethylene glycol in that on hydrate formation the pressure drop was not as rapid and from a visual point of view a layer of hydrates was not formed at the gas/liquid interface, in addition hydrate formation was mainly in the upper part of the cell. It would be necessary to conduct tests with the polymer alone to clarify what
influence it has upon the growth pattern. The tests with methane/distilled water and methane/aqueous solution ethylene glycol (1.5 mass%) showed little difference in terms of the pressure reduction with time on hydrate formation. From a visual point of view the test results were also similar in that a solid layer of hydrates formed at the gas/water interface and this prevented further significant hydrate formation. It may be that at higher degrees of sub-cooling than the 9°C used in these tests the addition of the ethylene glycol may lead to more hydrate formation. Of course there are other variables such as the concentration of ethylene glycol that may influence the growth pattern.

The tests with natural gas and HYTREAT® 04-049 and with methane and HYTREAT® 04-049 showed a similar pattern in that significant hydrate formation occurred. The growth pattern was similar in that hydrate formation started at the gas/liquid interface and continued mainly in the upper part of the cell removing the water from the lower part of the cell. In both cases small hydrate particles were seen in the liquid phase, however no solid layer of hydrates formed at the gas/liquid interface.

In the tests with the addition of PGPE to HYTREAT® 04-049 there was a clear difference compared to the test with HYTREAT® 04-049 alone in that the amount of hydrates formed from the pressure reduction data was significantly less with the PGPE. The visual observation of the growth pattern showed that the two cases were similar with no solid layer of hydrates forming and most of the hydrates forming in the upper part of the cell. It would appear that the effect of the PGPE was to slow the formation of hydrates in the hydrate mass forming in the upper part of the cell. In the test with LUVICAP® and PGPE the pressure time profile was similar to that seen with the HYTREAT® 04-049/PGPE test in that after initial hydrate formation the amount of hydrates formed was not large from the pressure/time data. The growth pattern was different in that a solid layer of hydrates formed at the gas/liquid interface and all of the water was not removed from the lower part of the cell. Gas bubbles appeared below the gas/liquid interface and hydrates formed at their surfaces.

From these tests it is clear that a variety of different hydrate growth patterns, both from pressure data and visual observations, are seen. Components such as ethylene
glycol, commonly used in hydrate inhibitor formulations, can influence the pattern of hydrate growth even at low concentrations. In addition additives such as PGPE showed a significant influence upon the hydrate growth pattern.
CHAPTER 5

HYDRATE NUCLEATION TESTS USING ULTRASONIC WAVES

5.1. INTRODUCTION

It has been suggested that an ideal kinetic hydrate inhibitor can be adsorbed on both nucleation sites and growth sites (Dimo Kashchiev and Abbas Firoozabadi, 2003). Combination analysis of Fast Fourier Transform (FFT) and amplitude of ultrasonic waves provides a unique method to investigate the performance of a kinetic inhibitor, i.e., how a kinetic inhibitor hinders hydrate nucleation by adsorbing on the nucleation sites and prevents hydrate growth by adsorbing on the growth sites. The method is believed to be helpful in understanding inhibition mechanism of kinetic inhibitors and designing better hydrate inhibitors. In the previous period of this project, by means of the ultrasonic rig, PVCap as a typical commercial kinetic inhibitor was investigated. It was found that PVCap prolonged the induction time of hydrate formation through both slowing down hydrate nucleation and delaying the catastrophic growth, mainly by preventing hydrate growth.

Based on synergism it may be plausible to assume that performance of kinetic inhibitors could be improved by adding some chemical additives as synergists (Cohen J.M., Wolf P.F., and Young W.D., 1998). In the previous progress report, the effect of tetrabutylammonium bromide (TBAB) as a synergist on the performance of PVCap was investigated using the ultrasonic rig. It appeared that TBAB did not show synergistic effect at static conditions, as the addition of 0.5 mass% of TBAB to 0.5 mass% of PVCap had a negative impact on the performance of PVCap in the natural gas-water system at static conditions.

During the last six-month period of the project, nucleation tests in the ultrasonic rig have been further extended to a new base polymer, the BASF advanced polymer. The effect of another synergist, Propylene, Glycol Propyl Ether (PGPE), on the performance of both PVCap and the advanced polymer was also investigated at static conditions. Finally, the kinetic feature of hydrate formation with PGPE was
examined. In all these tests, a natural gas with typical composition was used as hydrate former.

2. MATERIALS

Natural gas supplied by Air Product (Composition in Table 5.1)
LUVICAP® (40 mass% PVCap and 60 mass% ethylene glycol) supplied by Clariant Oil Services
The BASF Advanced Polymer (HYTREAT 04-049) supplied by Clariant Oil Services
Propylene Glycol Propyl Ether supplied by Aldrich Chemical Company, Inc.
Distilled water

Table 5.1  The Composition of  the natural gas used

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol%</th>
<th>Component</th>
<th>Mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>1.70</td>
<td>i-C₄</td>
<td>0.16</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.65</td>
<td>n-C₄</td>
<td>0.31</td>
</tr>
<tr>
<td>C₁</td>
<td>89.00</td>
<td>i-C₅</td>
<td>0.07</td>
</tr>
<tr>
<td>C₂</td>
<td>5.50</td>
<td>n-C₃ + C₆</td>
<td>0.11</td>
</tr>
<tr>
<td>C₃</td>
<td>1.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.3. METHOD AND PROCEDURE

In all the tests, the test cell was filled with 71 vol% of liquid phase and 29 vol% of gas phase to allow most of acoustic energy to propagate through liquid phase. This gave a constant volume ratio of gas to liquid as well, i.e., identical contact area of the hydrate former with water. The initial temperature and pressure conditions were also consistent in all the tests to exclude the undesirable effect of the initial thermodynamic conditions on gas hydrate nucleation and growth. All tests were conducted in bulk conditions and without stirring. Figure 5.1 shows the phase boundary of the natural gas hydrates and the injection conditions. The phase boundary was predicted using an in-house software.
Chapter 5  Hydrate Nucleation Tests Using Ultrasonic Waves

5.4. RESULTS AND DISCUSSIONS

In this period of the project, four series of tests have been conducted. The first aim of the work was to examine the inhibition characteristics of the BASF advanced polymer at static conditions. The next group of tests were carried out to investigate the effect of PGPE as a potential synergist on the performance of both PVCAP and the advanced polymer. The dependence of PGPE effect upon its concentration was tested in the third group of tests. The final test was conducted using PGPE alone to study hydrate inhibition effect of PGPE.

5.4.1 Inhibition Characteristics of The BASF Advanced Polymer

The BASF advanced polymer was tested at two different temperatures at about 115 bar and 4 °C (subcooling 15 °C) and 7 °C (subcooling 12 °C). Figure 5.2 shows the result of the test using 5 vol% of HYTREAT 04-049. Figure 5.2a shows the profiles of the system temperature, pressure and ultrasonic signals, and Figure 5.2b shows the

Figure 5.1  Hydrate phase boundary of the natural gas and the initial injection condition

The tests were carried out following same procedures. The cell was vacuumed first, and then a certain amount of the solution was sucked into the cell, finally, the natural gas was injected into the cell through a piston vessel until the desired pressure of about 125 bar was reached. The system was kept at 21 °C over night to equilibrate the system. Next day, the system was directly cooled down to the target temperature, 4 °C or 7 °C in the cooling bath depending on the test system. The system temperature and pressure were logged on a PC through RS-232 interface, and ultrasonic waveforms were displayed and recorded by the same PC.
response of temperature and pressure, and ultrasonic signals to hydrate formation in detail. In Figure 5.2a showing the profile of the system pressure, hydrates started catastrophic growth at 140 minutes (3.8 °C and 112 bar), and kept constantly growing at a pressure decline rate of 1.4 bar/hour for approximate 12 hours. In Figure 5.2b, FFT drop shows the onset of hydrate nucleation at 100 minutes. About 40 minutes of nucleation time was observed. There is no slow formation period between the

Figure 5.2  Hydrate nucleation and growth in the presence of 5 vol% HYTREAT 04-049, under 15 °C of subcooling

nucleation and the catastrophic growth. The rapid drop of FFT and amplitude in Figure 5.2 infers that both nucleation and growth were happening quickly in the liquid

5.4
phase. The test at 4 °C was repeated twice and the results were very similar. To remove the hydrate memory the system was heated to 35 °C for more than 12 hours. The nucleation started at about 100 minutes and hydrate formation happened rapidly at about 130 minutes, and last for 15 hours at a pressure decline rate of 1.2 bar/hour.

(a) The profile of the system temperature, pressure and the ultrasonic signals

(b) Response of the ultrasonic signals to hydrate nucleation in detail

Figure 5.3  Hydrate nucleation and growth in the presence of 5 vol% HYTREAT 04-049, under 12 °C of subcooling
To study the performance of HYTREAT 04-049 at lower degree of subcooling, another test was conducted at 7 °C, about 12 °C of subcooling. Figure 5.3a shows that hydrates started catastrophically forming at 730 minutes (6.8 °C and 114 bar), and that the growth continued for 30 hours at an average pressure decline rate of 1.7 bar/hour. In Figure 5.3b, hydrate nucleation was approximately identified at 140 minutes (6.8 °C and 115 bar) according to the tiny drop of the FFT and the fluctuation of the amplitude while the system temperature had been stable, which gives the nucleation time of about 10 hours.

5.4.2 Synergistic Effect of PGPE on Kinetic Inhibitors

The PGPE is a glycol ether with a formula of \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \). It is used as a solvent or coupling agent for cleaning products, with a boiling point of 140 °C to 160 °C, and a flash point of 48 °C. According to Cohen et al (1998) the glycol ethers improve the performance of PVCap and do not have hydrate inhibition effect without the polymer present.

In this study, the synergistic effect of PGPE on the BASF advanced polymer and PVCap was investigated. 5 vol% of the advanced polymer in water was tested in the presence of 1.5 mass% of PGPE (equivalent to 1.7 vol%). In the PVCap tests, 0.5 mass% of PVCap plus 0.75 mass% of PGPE was used. To examine the sustainability of the synergistic effect of PGPE under different degrees of subcooling, similarly, the tests were performed under 12 °C and 15 °C, respectively.

Figure 5.4 shows the result of the test on HYTREAT 04-049 + PGPE under 12 °C of subcooling. In Figure 5.4a it is very clear that the catastrophic hydrate formation started at 2432 minutes (6.8 °C and 113 bar), whilst the onset of hydrate nucleation was at 116 minutes (6.8 °C and 114 bar), which is indicated by slight decline of the FFT and amplitude in Figure 5.4b. The induction time is 39 hour under 12 °C of subcooling. This means that the addition of 1.5 mass% of PGPE to 5 vol% of HYTREAT 04-049 prolongs the nucleation time by 29 hours, compared with 10 hours with HYTREAT 04-049 alone in Figure 5.3.
Chapter 5  Hydrate Nucleation Tests Using Ultrasonic Waves

(a) The profile of the system temperature, pressure and the ultrasonic signals

(b) Response of the ultrasonic signals to hydrate nucleation in detail

Figure 5.4  Hydrate nucleation and growth in the presence of 5 vol% HYTREAT 04-049 plus 1.5 mass% of PGPE, under 12 °C of subcooling

To confirm this synergistic effect of PGPE, after the system was heated to 35 °C for more than 12 hours, the test was repeated. The induction time was 22 hours, significantly longer than 10 hours with HYTREAT 04-049 alone in Figure 5.3, although there is a difference of about 17 hours between the two repeating tests. It should be noted that there was no slow formation period between the nucleation onset and the catastrophic growth.
Chapter 5 Hydrate Nucleation Tests Using Ultrasonic Waves

(a) The profile of the system temperature, pressure and the ultrasonic signals

(b) Response of the ultrasonic signals to hydrate nucleation in detail

Figure 5.5 Hydrate nucleation and growth in the presence of 5 vol% HYTREAT 04-049 plus 1.5 mass% of PGPE, under 15 °C of subcooling

Figure 5.5 shows the result of the test with 5 vol% of HYTREAT 04-049 + 1.5 mass% of PGPE under 15 °C of subcooling. As can be seen in Figure 5.5b, the nucleation onset is indicated by the FFT drop at 108 minutes (6 °C and 112 bar), whilst, in Figure 5.5a, hydrates started catastrophically forming at 406 minutes (3.8 °C and 110 bar), at a pressure decline rate of 2.8 bar/hour. The nucleation time is 5 hours corresponding to 40 minutes of the test with HYTREAT 04-049 alone in Figure 5.2. This means that PGPE also improved the performance of the BASF advanced polymer under high subcooling.
To examine the synergistic effect of PGPE on PVCap two pairs of tests were carried out, one with 0.5 mass% of PVCap alone, and another one with 0.5 mass% of PVCap plus 0.75 mass% of PGPE. Each pair of the tests was performed under 15 °C and 12 °C of subcooling, respectively. Under 12 °C of subcooling, the two tests neither with 0.5 mass% of PVCap alone nor with 0.5 mass% of PVCap plus 0.75 mass% of PGPE had no hydrate formation identified within 48 hours.

Figure 5.6  Hydrate nucleation and growth in the presence of 0.5 mass% PVCap alone, under 15 °C of subcooling

Figure 5.6 shows the result of the test using 0.5 mass% of PVCap alone. In Figure 5.6a, it can be seen that hydrates started slow formation at 156 minutes (4 °C and 111
bar), followed by catastrophic growth at 420 minutes (4 °C and 105 bar), and hydrates kept growing for about 48 hours at an average pressure decline rate of 0.85 bar/hour. Hydrate nucleation started at around 106 minutes (7 °C and 114 bar), which gives nucleation time of about half an hour.

(a) The profile of the system temperature, pressure and the ultrasonic signals

(b) Response of the ultrasonic signals to hydrate nucleation in detail

Figure 5.7  Hydrate nucleation and growth in the presence of 0.5 mass% PVCap plus 0.75 mass% of PGPE, under 15 °C of subcooling

Figure 5.7 shows the result using 0.5 mass% of PVCap plus 0.75 mass% of PGPE. As shown in Figure 5.7a, hydrates started slowly forming at 460 minutes (3.9 °C and 111 bar) and continuously growing at pressure decline rate of 0.16 bar/hour, and no
catastrophic growth appeared within 48 hours. Figure 5.7b shows that the nucleation onset at 60 minutes (12 °C and 119 bar) was identified by FFT and amplitude of ultrasonic waves. The nucleation time was near 7 hours. By comparison with the test using 0.5 mass% of PVCap alone, it can be found that, 0.75 mass% of PGPE prolongs the nucleation time by 6 hours and slows down hydrate growth by 4 times of the pressure decline rate, from 0.85 bar/hour to 0.16 bar/hour.

5.4.3 Dependence of Synergistic Effect of PGPE on Its Concentration

Besides the optimum concentration of 0.75 mass% suggested by Cohen, et al, two more extreme PGPE concentrations were tried to study the dependence of synergistic effect of PGPE on its concentration. For simplification the same PVCap concentration (0.5 mass%) was used, and the tests were consistently conducted under 15 °C of subcooling.

As can be seen in Figure 5.8, the result using 0.5 mass% of PVCap plus 1.5 mass% of PGPE is similar to that of the test adding 0.75 mass% of PGPE to 0.5 mass% of PVCap in Figure 5.7. Hydrates started nucleation at 50 minutes (13 °C and 119 bar), slow formation approximately at 130 minutes (4.1 °C and 110 bar), and continuously grew during the whole test of more than 48 hours. By comparison to the test with addition of 0.75 mass% of PGPE to 0.5 mass% of PVCap in Figure 5.7, one improvement is that in the test with addition of 1.5 mass% of PGPE hydrate growth is even slower, 0.16 bar/hour in the test with addition of 0.75 mass% of PGPE and 0.071 bar/hour in the test with addition of 1.5 mass% of PGPE. This may suggest that high concentration of PGPE could prevent hydrate growth better, but little improvement on nucleation inhibition.
Chapter 5 Hydrate Nucleation Tests Using Ultrasonic Waves

In Figure 5.9 the result of the test adding 0.25 mass% of PGPE to 0.5 mass% of PVCap is close to that of the test with 0.5 mass% of PVCAP alone in Figure 5.6. There were nucleation indication at 113 minutes (7 °C and 113 bar), then slow hydrate formation staring at 140 minutes (4 °C and 111 bar), followed by a little quicker growth starting at 250 minutes (3.9 °C and 110 bar), and hydrates kept forming within the entire test period of 46 hours, at an average pressure decline rate of 0.35 bar/hour which is approximately 2 times lower than 0.85 bar/hour in the test with 0.5 mass% of PVCap alone. This result may suggest that low concentration of PGPE is not...
sufficient to improve nucleation inhibition, but could reduce hydrate formation rate to some extent.

![Graph showing system temperature, pressure, and ultrasonic signals](image)

(a) The profile of the system temperature, pressure and the ultrasonic signals

![Graph showing response of ultrasonic signals to hydrate nucleation](image)

(b) Response of the ultrasonic signals to hydrate nucleation in detail

Figure 5.9  Hydrate nucleation and growth in the presence of 0.5 mass% of PVCap plus 0.25 mass% of PGPE, under 15 °C of subcooling

### 5.4.4 Hydrate Formation in The Presence of PGPE Alone

To examine how gas hydrates form in the natural gas-water system in the presence of PGPE alone, one test was conducted using 1.5 mass% of PGPE under 15 °C of subcooling. Figure 5.10 shows the result. The onset of hydrate nucleation is indicated by the continuous drop of the FFT and amplitude at 92 minutes (8 °C and 114 bar),

5.13
slight decline of the system pressure with rapid drop of the FFT and amplitude suggested the start of hydrate slow formation at 120 minutes (5 °C and 111 bar), the growth rate increased a little bit at 570 minutes (3.9 °C and 108 bar). Hydrates was continuously forming at an average pressure decline rate of 0.16 bar/hour for 48 hours.

Figure 5.10 Hydrate formation in the presence of 1.5 mass% of PGPE alone, under 15 °C of subcooling

With PGPE alone, the most significant feature of gas hydrate formation is that the FFT and amplitude of ultrasonic signals rapidly dropped with time, even though the hydrates growth was very slow. This is significantly distinct from the performance of
PVCap in Figure 5.6 through 5.9, similar with those in the tests with the BASF advanced polymer in Figure 5.2 through 5.5, independent of PGPE concentration in the solution. As the FFT and amplitude of the ultrasonic signals dominantly respond to the phase transition in the bulk of liquid in the test cell, in the presence of both HYTREAT 04-49 and PGPE it is likely that phase transition, including hydrate nucleation and formation of tiny crystals, rapidly spread from the gas-liquid interface into the bulk of liquid, once hydrates started formation. On the contrary, hydrate formation with PVCap could not spread quickly into the liquid phase, as shown by the relatively slow decline of the FFT and amplitude, which suggested that PVCap prevents gas hydrates from growing more effectively.

5.5. SUMMARY

Based on the above tests conducted in the ultrasonic, the main results are summarized in Table 5.2, and some conclusions may be reached as below.

(1) The BASF advanced polymer HYTREAT 04-049 shows different inhibition feature from that of PVCap. The advanced polymer inhibited hydrate formation almost completely before the catastrophic growth started, while hydrates grew very rapidly once formation starts. In Table 5.2, this is shown as the longer nucleation time and higher rate of hydrate formation, compared with those of the PVCap tests. On the other hand, PVCap is likely to hinder hydrate growth rather than nucleation, which is shown in Table 5.2 as shorter nucleation time and significantly lower rate of hydrate growth. In general, HYTREAT 04-049 is good at preventing hydrate nucleation, whilst PVCap is relatively better to inhibit hydrate growth.

Table 5.2 also shows that PVCap has higher sustainability under high subcooling than HYTREAT 04-049 does.

(2) PGPE as a synergist can significantly improve the performance of both HYTREAT 04-049 and PVCap. As can be seen in Table 5.2, addition of 1.5 mass% of PGPE to 5 vol% of the BASF advanced polymer increased the induction time by 4 hours under 15 °C of subcooling, and by 29 hours under 12 °C. Addition of 0.75 mass% of PGPE to 0.5 mass% of PVCap increased the induction time by 6 hours under 15 °C of subcooling, and delayed the catastrophic growth by more than 36 hours.
This synergistic effect of PGPE was achieved under static conditions. However, the flowing tests performed in the high pressure micromodel also showed consistent results. (Please see Chapter 2)

(3) Synergistic effect of PGPE on the performance of the both polymers certainly depends on its concentration. In Table 5.2, by comparison with the test with 0.5 mass% of PVCap alone, it can be seen that the catastrophic growth of hydrate formation was significantly delayed by the addition of PGPE, and the higher the concentration of PGPE, the more significant the improvement.

(4) According to the test with 1.5 mass% of PGPE, shown in Figure 5.10, it seems that PGPE shows some hydrate inhibition effect at static conditions. In the presence of PGPE alone, phase transition rapidly spread from the interface between gas phase and liquid phase into the bulk of liquid, once hydrates started formation.

REFERENCES


Table 5.2 Summary of the test results

<table>
<thead>
<tr>
<th>Kinetic Inhibitor</th>
<th>Nucleation time /hour</th>
<th>Slow formation period /hour</th>
<th>Catastrophic growth delay /hour</th>
<th>Formation rate bar/hour</th>
<th>FFT &amp; Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 °C</td>
<td>12 °C</td>
<td>15 °C</td>
<td>12 °C</td>
<td>15 °C</td>
</tr>
<tr>
<td>BBP 5 vol%</td>
<td>&lt; 1</td>
<td>10</td>
<td>No</td>
<td>No</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>BBP+PGPE 5 v%+1.5 m%</td>
<td>5</td>
<td>39</td>
<td>No</td>
<td>No</td>
<td>5</td>
</tr>
<tr>
<td>PVCAP 0.5 mass%</td>
<td>&lt; 1</td>
<td>not appeared</td>
<td>4</td>
<td>not appeared</td>
<td>5</td>
</tr>
<tr>
<td>1 mass%*</td>
<td>2</td>
<td>~</td>
<td>39</td>
<td>~</td>
<td>41</td>
</tr>
<tr>
<td>PVCAP (0.5 0.25 mass%) +</td>
<td>&lt; 1</td>
<td>~</td>
<td>2</td>
<td>~</td>
<td>2</td>
</tr>
<tr>
<td>mass%</td>
<td>0.75 mass%</td>
<td>7</td>
<td>not appeared</td>
<td>&gt; 40</td>
<td>not appeared</td>
</tr>
<tr>
<td>PGPE 1.5 mass%</td>
<td>1</td>
<td>~</td>
<td>&gt; 65</td>
<td>~</td>
<td>not appeared</td>
</tr>
<tr>
<td>PGPE 1.5 mass%</td>
<td>&lt; 1</td>
<td>~</td>
<td>7</td>
<td>~</td>
<td>8</td>
</tr>
</tbody>
</table>

Notes:

(1) Nucleation time is defined as a time interval between the FFT/amplitude response and the first detectable pressure drop.
Slow formation period is defined as a time interval between the first detectable pressure drop and the onset of catastrophic pressure drop.
Delay of catastrophic growth is defined as a time gap between the onsets of nucleation and catastrophic growth.
(2) Hydrate formation rate is represented by an average pressure decline rate approximately determined over hydrate growing period.
(3) It is suggested that 5 vol% of the BASF advanced polymer (HYTREAT 04-049) is equivalent to 1 mass% of PVCap.
(4) 12 °C and 15 °C represent the degree of subcooling.
(5) The natural gas and distilled water were used in all tests.
* The result using 1 mass% of PVCap was reported in the previous report, March 2003 to Nov 2003.
CHAPTER 6

APPLICATION OF HELICAL TUBE MIXER IN EVALUATION OF ANTI-AGGLOMERANTS

6.1. INTRODUCTION

The study of anti-agglomerants (AA) along with kinetic hydrate inhibitors (KHI) was included in the proposal of the current LDHI project previously. In the previous progress reports (November 2003 and June 2004) after presentation of a literature survey on anti-agglomerants, which included development of AA chemicals, their field applications and laboratory techniques for testing them, the experimental facilities in the Heriot-Watt University for evaluation of them were detailed. In addition to application of Glass Micromodels set up, torque measurement in a kinetic rig was used for evaluation of anti-agglomerants. However, it was observed that in some tests, after hydrate formation, the torque was decreased because of centrifugal force effect of the paddle type impeller on the hydrate particles, which push them toward the rig wall. In order to overcome that problem, in the last steering committee meeting, it was suggested to replace the existing rig impeller with a helical tube, which by rotation in the bulk of fluids may simulate flow in a pipeline. In the following sections the preliminary experiments carried out in a kinetic rig with a helical tube impeller, in the presence and absence of an anti-agglomerant in condensate-water-natural gas system are detailed.

6.2. MATERIAL

Natural gas supplied by Air Product (Composition in Table 6.1)
Anti-Agglomerant labelled as (HT03-186) and provided by Clariant Oil Services
Two natural gas condensates: North Sea East Frigg field condensate provided by Clariant Oil Services and another North Sea field (Norwegian Sector of the North Sea) natural gas condensate labelled as LTB-98-1C and provided by Reservoir Fluid Research Group at Heriot-Watt University.
Distilled water
Table 6.1. Composition of the natural gas (LAB-NG) used in the experiments

<table>
<thead>
<tr>
<th>Component</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>i-C₄</th>
<th>n-C₄</th>
<th>i-C₅</th>
<th>n-C₅⁺</th>
<th>N₂</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol%</td>
<td>89.0</td>
<td>5.50</td>
<td>1.50</td>
<td>0.16</td>
<td>0.31</td>
<td>0.07</td>
<td>0.11</td>
<td>1.70</td>
<td>1.65</td>
</tr>
</tbody>
</table>

### 6.2. KINETIC RIG TESTS

The effectiveness of the Kinetics Rig in sensing the rheological changes and stirrer blockage in different fluid systems with and without AA LDHIs was tested in a preliminary programme and reported in the last progress report. In this series of tests, a Kinetics Rig with a volume of 2400 ml was modified to facilitate the AA LDHI testing. A specially designed helical tube stirrer was used for mixing and torque measurement. The stirrer is a helical copper tube (ID= 7.7mm), which is fitted into the testing cell. During the experiments, the rheology of the hydrate slurry is monitored by measuring the torque applied on the stirrer shaft. The applied torque will be a function of fluid friction inside and outside of the helical tube stirrer. After hydrate formation, torque will increase. However, if the hydrates formed are dispersed into oil/condensate phase as small particles as expected when an AA-LDHI is present, torque increase will be limited. Otherwise, large torque increase can be observed. In all the experiments, a solution of 33 volume% of distilled water in condensate was first loaded into the test cell, and then natural gas was charged into the cell up to the required pressure. In the tests with AA, it was pre-mixed with water phase before loading to the testing cell. The system was then cooled down to form hydrate and the torque along with pressure and temperature were measured and recorded during the test.

#### 6.2.1. EXPERIMENTS ON NATURAL GAS-WATER SYSTEM

Three blank tests conducted on the natural gas-water system at different rates of mixing to study the torque behaviour before and after hydrate formation. In all the experiments, the test started at around 120 bar and 34 °C and the system was cooled down to 3-4 °C to form hydrate. After some time the system was heated up to 34 °C to
dissociate the hydrates, and the pressure, temperature and torque profiles were recorded. Figure 6.1 present the results of test at 100 rpm. As seen, at 34 °C the torque value is 16 (arbitrary unit), by cooling down the system to 3.5 °C, hydrate started to form at around 100 bar and 4.5 °C (14 °C subcooling). The rate of hydrate growth was slow (as seen from slow pressure drop) and the torque was increased to 30. After one day, the pressure dropped to 85 bar and the torque was fluctuating between 26-30. The slow rate of hydrate growth may be attributed to poor mixing of the system. After heating the system up to 34 °C, the hydrate dissociated and pressure increased to 120 bar and torque decreased to its primary magnitude 16. The above test repeated with 200 rpm and the resulted profiles are presented in Figure 6.2. In that test because of higher rate of mixing, hydrate formed at lower degree of subcooling (100 bar and 10.5 °C equivalent to 8 °C subcooling) than that of test with 100 rpm. In addition more hydrate formed (pressure dropped to 42 bar) with higher rate of growth. After hydrate formation the torque was increased to 89 and after one hour it dropped to 42 (53% reduction). The torque stabilised at 42, where no more hydrate formed for 11 hours. By heating up the system to 34 °C the torque decreased to its primary magnitude 23 again. In the test with 400rpm (Figure 6.3), as expected the primary torque at 34 °C (37) was higher than those of two previous tests (16 and 23 respectively). After hydrate formation at around 100 bar and 11.5°C (7 °C subcooling), the torque increased to 125 and stabilised there for three hours. During the next 9 hours, after when the system heated up, the torque was decreased slowly to 97 (23% reduction).

![Graph](image)

Figure 6.1. Pressure, temperature and torque profiles for NG-water system, rpm=100.
The reason of torque reduction after hydrate formation and reaching to its maximum level, is not clear yet and needs further investigation. On the basis of above tests, rate of mixing 400 rpm was selected for the experiments with anti-agglomerant because at 100 rpm the mixing is poor and hydrate formation is slow and at 200 rpm the torque reduction after hydrate formation is considerable.

![Figure 6.2](image1.png)  
Figure 6.2. Pressure, temperature and torque profiles for NG-water system, rpm=200.

![Figure 6.3](image2.png)  
Figure 6.3. Pressure, temperature and torque profiles for NG-water system, rpm=400.
6.2.2. EXPERIMENTS ON NATURAL GAS-CONDENSATE-WATER SYSTEM

6.2.2.1. North Sea Field Natural Gas Condensate

In the second series of experiments, which were repetition of the above test procedure with a rate of mixing of 400 rpm, a solution of 33 volume % water in a North Sea field natural gas condensate (labelled as LTB98-1-C) was used in the presence and absence of an anti-agglomerant (HT03-186). The first two tests were carried out in the absence of AA. The profiles of the first test are shown in Figure 6.4. As shown in Figure 6.4, the test started at 117 bar and 34 °C, where torque was about 35. The system was then cooled down and when hydrate formed at about 12 °C and 100 bar (6.5 °C subcooling with respect to natural gas-water hydrate phase boundary), torque was increased to 154 and after one hour it stabilised at 145. By increasing the temperature to 34°C, torque was reduced to 35. It should be noted that in test with condensate, after hydrate formation the torque is stable while in the test with natural gas-water (Figures 6.2-6.3) the torque was decreasing slowly. By repeating the above test, good repeatability of experiment was observed. The results of the repeat test are presented in the Appendix B (Figure 45). It is worth to notice that at similar test conditions, in the presence of a condensate phase less hydrate formed than that in NG-water test (compare Fig.6.3 with Fig 6.4). This may be attributed to natural inhibition of condensate phase.
The above tests were repeated in the presence of 2.5 volume % of HT03-186. The results of the first test are shown in Figure 6.5 and the results of the repeat test are presented in the Appendix B (Figure 46). As shown in Figure 6.5, after hydrate formation (at 7.5°C and 98 bar equivalent to 10.9°C subcooling with respect to natural gas-water hydrate phase boundary) torque increased to 128 and then decreased to 122 within few hours, after when the system heated up. As expected, in comparison to the test without AA (Figure 6.4), after hydrate formation the maximum torque was decrease by 19% (compare the maximum torque with that of Figure 6.4).

The fact that the amount of hydrate formed is much higher than that of test without AA (Figure 6.4) and comparable to that of NG-water system test (Figure 6.3), shows that the AA used is hydrate promoter.

6.2.2.2.East Frigg Field Natural Gas Condensate

The above tests in section 6.3.2.1 were repeated with another condensate, East Frigg field natural Gas Condensate. The results of the test in the absence of anti-agglomerant (blank test) is presented in Figure 6.6. As seen in the Figure 6.6, hydrate
formed at 10.5°C and 100 bar (8 °C subcooling with respect to natural gas-water hydrate phase boundary) and torque was increased to 148 from its initial value 28 at 34 °C. Within three hours when the pressure and temperature of the system were stable, torque was decreased to 135. Again, the amount of hydrate formed is less than that of NG-water system at similar test conditions (compare with Figure 6.3). The results of the test in the presence of anti-agglomerant (HT03-186) is presented in Figure 6.7. At 34 °C the torque was about 29 and after hydrate formation at 100 bar

![Figure 6.6](image1.png)

**Figure 6.6.** Pressure, temperature and torque profiles for Condensate (East Frigg field) NG-water, rpm=400.

![Figure 6.7](image2.png)

**Figure 6.7.** Pressure, temperature and torque profiles for Condensate (East Frigg field)
NG-water and 2.5 vol% HT03-186, rpm=400.

and 10.5 °C (8 °C subcooling with respect to natural gas-water hydrate phase boundary) it was increased to 136 and after 2 hours it stabilised at 112. The stable torque after hydrate formation in the presence of AA is 20% less than that of test without AA. This is while higher amount of hydrate formed in the presence of AA.

6.3. SUMMARY

In this study, the application of a helical tube mixer in a kinetic rig with for evaluation of anti-agglom erants in condensate-water-natural gas systems was tested. By the experiments carried out in natural gas-water system at different rates of mixing (rpm), the rate of mixing 400 rpm was selected for further tests in condensate systems because of better mixing efficiency and more stable torque responses to the rheologicla changes of the system. The torque measurement results in the experiments were carried out with two different types of condensate and natural gas-water systems in the presence and absence of an anti-agglomerants showed promising results and applicability of the method. After hydrate formation reasonable torque stability after hydrate formation was observed in condensate-natural gas-water systems. For both condensate systems tested, although the amounts of hydrate formed in the presence of anti-agglomerant were much higher than those tests without AA, the torque values after hydrate formation in the presence of anti-agglomerant appeared to be around 20% less than that of in the absence of AA (for the tests conducted on this fluid system). Furthermore, it was noticed that in the presence of condensate phase less amount of hydrate forms in comparison to the tests without condensate ate similar conditions.
Appendix A
Experimental Equipment at the Centre for Gas Hydrate Research

Hydrate Rig-1

Main applications:
1. Measuring the hydrate stability zone of various fluid systems (e.g., gas, gas condensate and oil systems).
2. Determining the effect of various hydrate inhibitors (e.g., salts and/or organic inhibitors) on the hydrate stability zone.
3. Determining the hydrate characteristics of water or oil based drilling fluids.
4. Investigating the kinetics of gas hydrate formation and dissociation.
5. Measuring the amount and composition of equilibrated phases (including gas hydrates) in gas-water-hydrate systems.

Operating conditions:
Pressure: up to 10,000 psia (70 MPa)
Temperature: from –35 to 75 ºC

Description:
Rig-1 consists of a high-pressure cell (70MPa) with a variable volume which is adjusted by adding or withdrawing mercury using a pump. Test fluids are confined between an optically-clear quartz glass tube and the metal body of the cell. A borescope fitted with a camera can be passed into the quartz tube in order to view the cell contents. The temperature of the cell is controlled to within 0.05 ºC. The pressure in the cell is monitored by two pressure transducers with an estimated accuracy of ±0.007 MPa. A computer is used to collect data and control the system.

The experimental set-up can be used for investigating the effects of thermodynamic hydrate inhibitors (electrolytes and organic inhibitors) and drilling mud constituents on hydrate stability zone and kinetics of gas hydrate formation and dissociation. The rig could be used for measuring the amount and composition of various phases (including gas hydrates) in multiphase equilibria. The data obtained provides means for development of empirical correlations and validation of numerical models.
Ultra High Pressure Rig

Main applications:
1. Measuring the hydrate stability zone of various fluid systems (e.g., gas, gas condensate and oil systems).
2. Determining the effect of various hydrate inhibitors (e.g., salts and/or organic inhibitors) on the hydrate stability zone.
3. Investigating the kinetics of gas hydrate formation and dissociation.
4. Water-hydrocarbon phase equilibria
5. Water and/or hydrocarbon dew point and bubble point measurements

Operating conditions:
Pressure: up to 30,000 psia (200 MPa)
Temperature: from –30 ºC to 80 ºC

Description:
The Ultra High Pressure Rig was commissioned in 2003 for measuring hydrate stability zones at very high pressures conditions. It consists of a 45cc cell with a maximum operating pressure of 200MPa. The cell temperature is controlled by circulating coolant inside a jacket surrounding the cell, giving an operating temperature of -30 to 80 ºC. The cell has four ports, two of which are used for high-pressure electric feed-throughs enabling a Quartz Crystal Microbalance (QCM) to be mounted inside the cell. A third port is used for a PRT to monitor the temperature (accurate to 0.1 ºC), while the fourth port is used for pressure measurement with a Quartzdyne pressure transducer (accuracy of 0.007MPa) and for loading fluids into the cell. The cell is mounted on a compressed air powered rocking mechanism for mixing of contents. Cell pressure, temperature and QCM resonant frequency are recorded by a PC.
Main applications:
1. Evaluating the performance of Kinetic Hydrate Inhibitors (KHIs), by measuring the induction time, rate of hydrate formation, pressure drop due to hydrate formation.
2. Evaluating the performance of Anti-Agglomerants (AA) in preventing gas hydrate problems, by measuring the torque applied to the mixer, and rate of hydrate formation.
3. Determining the effect of natural inhibitors and emulsions in preventing gas hydrate problems.
4. Simulating various production scenarios, such as, shut-downs and start-ups.
5. Investigating the kinetics of gas hydrate formation and dissociation.
6. Measuring the hydrate stability zone of various fluid systems (e.g., gas, gas condensate and oil systems).
7. Determining the effect of various hydrate inhibitors (e.g., salts and/or organic inhibitors) on the hydrate stability zone.
8. Qualitative measurement of viscosity and transportability of fluids containing hydrates and/or wax, as well as start-ups.

Operating conditions:
Pressure: up to 6,000 psia (40 MPa)
Temperature: from –30 to 75 ºC

Description:
The rig consists of a high-pressure vessel (40 MPa) with a 2.4 litre volume. The cell temperature is controlled by circulating coolant inside a jacket in the cell wall, and measured by a thermocouple to an accuracy of 0.1 ºC. The cell pressure is monitored by a quartzdyne pressure transducer (accuracy of 0.007 MPa). A magnetic stirrer with adjustable rotation speed (i.e., rpm) is used to agitate the test fluids. The torque required to drive the stirrer at a constant speed is measured and related to the viscosity of the system. A computer is used to collect data for pressure, temperature and torque.
Kinetics Rig-2

Main applications:
1. Evaluating the performance of Kinetic Hydrate Inhibitors (KHIs), by measuring the induction time, rate of hydrate formation, pressure drop due to hydrate formation.
2. Evaluating the performance of Anti-Agglomerants (AA) in preventing gas hydrate problems, by measuring the torque applied to the mixer, and rate of hydrate formation.
3. Determining the effect of natural inhibitors and emulsions in preventing gas hydrate problems.
4. Simulating various production scenarios, such as, shut-downs and start-ups.
5. Investigating the kinetics of gas hydrate formation and dissociation.
6. Measuring the hydrate stability zone of various fluid systems (e.g., gas, gas condensate and oil systems).
7. Determining the effect of various hydrate inhibitors (e.g., salts and/or organic inhibitors) on the hydrate stability zone.
8. Qualitative measurement of viscosity and transportability of fluids containing hydrates and/or wax, as well as start-ups.

Operating conditions:
- Pressure: up to 10,000 psia (70 MPa)
- Temperature: from –30 °C to 75 °C

Description:
Kinetic Rig-2 has very much similar application as the Kinetic Rig-1. It consists of a high-pressure vessel (69 MPa) with a 0.5 litre volume. The cell temperature is controlled by circulating coolant inside a constant temperature bath, it has an operating temperature range of -30 to 75 °C and this is measured by a thermocouple to an accuracy of 0.1 °C. The cell pressure is monitored by a pressure transducer (accuracy of 0.015 MPa). A magnetic stirrer with adjustable rotation speed (i.e., rpm) is used to agitate the test fluids. The torque required to drive the stirrer at a constant speed is measured and related to the viscosity of the system. A computer is used to collect data for pressure, temperature and torque.
Main applications:
1. Evaluating the performance of Kinetic Hydrate Inhibitors (KHIs), by measuring the induction time, rate of hydrate formation, pressure drop due to hydrate formation.
2. Investigating the kinetics of gas hydrate formation and dissociation.
3. Measuring the hydrate stability zone of various fluid systems (e.g., gas, gas condensate and oil systems).
4. Determining the effect of various hydrate inhibitors (e.g., salts and/or organic inhibitors) on the hydrate stability zone.

Operating conditions:
- Pressure: up to 4,500 psia (30 MPa)
- Temperature: from –30 to 75 ºC

Description:
Kinetic Rig-3 has similar application as the Kinetic Rigs-1 and 2. It consists of a high pressure cell (30MPa) with a volume of 500cc, a magnetic bar for stirring, coolant jacket and temperature/pressure recording equipment controlled by a computer. It has an operating range of –30 to 75 ºC with temperature being controlled to within 0.05ºC. Temperature is measured by PRTs and pressure by Quartzdyne pressure transducers.
Main applications:
1. Evaluating the performance of Kinetic Hydrate Inhibitors (KHI's), by measuring the induction time, rate of hydrate formation, pressure drop due to hydrate formation.
2. Evaluating the performance of Anti-Agglomerants (AA) in preventing gas hydrate problems, by measuring the torque applied to the mixer, and rate of hydrate formation.
3. Determining the effect of natural inhibitors and emulsions in preventing gas hydrate problems.
4. Simulating various production scenarios, such as, shut-downs and start-ups.
5. Investigating the kinetics of gas hydrate formation and dissociation.
6. Measuring the hydrate stability zone of various fluid systems (e.g., gas, gas condensate and oil systems).
7. Determining the effect of various hydrate inhibitors (e.g., salts and/or organic inhibitors) on the hydrate stability zone.
8. Qualitative measurement of viscosity and transportability of fluids containing hydrates and/or wax, as well as start-ups.

Operating conditions:
Pressure: up to 4,500 psia (30 MPa)
Temperature: from –35 °C to 75 °C

Description:
Kinetic Rig-4 has very much similar application as the Kinetic Rigs-1 and 2. It consists of a high-pressure vessel (30 MPa) with a 0.25 litre volume. The cell temperature is controlled by circulating coolant inside a constant temperature bath, it has an operating temperature range of -35 to 75 °C and this is measured by a thermocouple to an accuracy of 0.1 °C. The cell pressure is monitored by a pressure transducer (accuracy of 0.015 MPa). A magnetic stirrer with adjustable rotation speed (i.e., rpm) is used to agitate the test fluids. The torque required to drive the stirrer at a constant speed is measured and related to the viscosity of the system. A computer is used to collect data for pressure, temperature and torque.
The rig is very similar to Kinetic Rig-1. The main difference is in its mixing system and the improved ability to measure the transportability of fluids in the presence of wax and/or hydrates. Main applications:

1. Evaluating the performance of Kinetic Hydrate Inhibitors (KHIs), by measuring the induction time, rate of hydrate formation, pressure drop due to hydrate formation.
2. Evaluating the performance of Anti-Agglomerants (AA) in preventing gas hydrate problems, by measuring the torque applied to the mixer, and rate of hydrate formation.
3. Determining the effect of natural inhibitors and emulsions in preventing gas hydrate problems.
4. Simulating various production scenarios, such as, shut-downs and start-ups.
5. Investigating the kinetics of gas hydrate formation and dissociation.
6. Measuring the hydrate stability zone of various fluid systems (e.g., gas, gas condensate and oil systems).
7. Determining the effect of various hydrate inhibitors (e.g., salts and/or organic inhibitors) on the hydrate stability zone.
8. Qualitative measurement of viscosity and transportability of fluids containing hydrates and/or wax, as well as start-ups.

**Operating conditions:**
- Pressure: up to 6,000 psia (40 MPa)
- Temperature: from –30 to 75 ºC

**Description:**
The rig consists of a high-pressure vessel (40 MPa) with a 2.4 litre volume. The cell temperature is controlled by circulating coolant inside a jacket in the cell wall, and measured by a thermocouple to an accuracy of 0.1 ºC. The cell pressure is monitored by a quartzdyne pressure transducer (accuracy of 0.007 MPa). A magnetic stirrer with adjustable rotation speed (i.e., rpm) is used to agitate the test fluids. The torque required to drive the stirrer at a constant speed is measured and related to the viscosity of the system. A computer is used to collect data for pressure, temperature and torque.
**Kinetic Rig-6 (with Visual Capabilities)**

This rig will have similar capabilities to other kinetic rigs with the extra benefit of visual observation through its four window. Main applications:

1. Evaluating the performance of Kinetic Hydrate Inhibitors (KHIs), by measuring the induction time, rate of hydrate formation, pressure drop due to hydrate formation.
2. Evaluating the performance of Anti-Agglomerants (AA) in preventing gas hydrate problems, by measuring the torque applied to the mixer, and rate of hydrate formation.
3. Determining the effect of natural inhibitors and emulsions in preventing gas hydrate problems.
4. Simulating various production scenarios, such as, shut-downs and start-ups.
5. Investigating the kinetics of gas hydrate formation and dissociation.
6. Measuring the hydrate stability zone of various fluid systems (e.g., gas, gas condensate and oil systems).
7. Determining the effect of various hydrate inhibitors (e.g., salts and/or organic inhibitors) on the hydrate stability zone.
8. Qualitative measurement of viscosity and transportability of fluids containing hydrates and/or wax, as well as start-ups.

**Operating conditions:**

- **Pressure:** up to 6,000 psia (40 MPa)
- **Temperature:** from –30 to 75 ºC

**Description:**
The rig consists of a high-pressure vessel (40 MPa) with a 300 cc volume with four visual windows. The cell temperature is controlled by circulating coolant inside a jacket in the cell wall, and measured by a thermocouple to an accuracy of 0.1 ºC. The cell pressure is monitored by a quartzdyne pressure transducer (accuracy of 0.007 MPa). A magnetic stirrer with adjustable rotation speed (i.e., rpm) is used to agitate the test fluids. The torque required to drive the stirrer at a constant speed is measured and related to the viscosity of the system. A computer is used to collect data for pressure, temperature and torque.
**Constant Volume High Pressure Quartz Crystal Microbalance Rig**

**Main applications:**
1. Measuring wax appearance and disappearance temperatures for stabilised and live fluid systems.
2. Effect coating and surface conditions on solid deposition (wax, scale, and asphaltene) inside pipelines.
3. Evaluating the performance of wax inhibitors and cloud point depressants.
4. Determining the effect of various hydrate inhibitors (e.g., salts and/or organic inhibitors) on the hydrate stability zone.
5. Investigating the kinetics of gas hydrate (or wax) formation and dissociation.
6. Measuring the hydrate stability zone of various fluid systems (e.g., gas, gas condensate and oil systems).

**Operating conditions:**
- Pressure: up to 6,000 psia (40 MPa)
- Temperature: from –35 to 75 °C

**Description:**
The set-up consists of a small volume (40cc) cell surrounded by a water jacket connected to a variable temperature circulator. The cell contents can be mixed by a magnetic stirrer. The cell is fitted with high pressure feed throughs for connection to microbalance device.
**Constant Volume Low Pressure Quartz Crystal Microbalance Rig**

**Main applications:**
1. Measuring wax appearance and disappearance temperatures for stabilised fluid systems.
2. Effect coating and surface conditions on solid deposition (wax, scale, and asphaltene) inside pipelines.
3. Evaluating the performance of wax inhibitors and cloud point depressants.

**Operating conditions:**
- Pressure: Atmospheric pressure
- Temperature: from −30 to 80 °C

**Description:**
The Rig comprised of a small volume (15cc) vessel surrounded by a water jacket connected to a circulating heater/cooler bath allowing the temperature to be controlled within an operating range of -30 to 80 °C with an accuracy of 0.1°C. This Rig is used for non-visual measurements at atmospheric pressure. The cell is mounted on a magnetic stirrer, with a spinning magnet inside the cell providing mixing. The resonant frequency of the QCM is monitored using an impedance/gain-phase analyser.

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**Variable Volume High Pressure Quartz Crystal Microbalance Rig**

**Main applications:**
1. Measuring dew point and bubble point of hydrocarbon system by pressure search.
2. Investigating water-hydrocarbon phase equilibria.

**Operating conditions**
- Pressure: up to 6,000 psia (40 MPa)
- Temperature: -20 °C to 80 °C

**Description:**
The rig is comprised of a variable volume (maximum 150cc) high pressure (maximum pressure 40MPa) piston cell. The cell is controlled by a constant temperature bath. The set-up has an operating temperature range of (-20) to 80 °C. Cell pressure is measured by a Quartzdyne pressure transducer and temperature by a PRT. The accuracy of the pressure measurement is 0.007MPa and the temperature measurement is 0.1°C. The cell is fitted with high-pressure electric feed-throughs which are connected to a QCM that is mounted inside the cell. The resonant frequency of the QCM is monitored using an impedance/gain-phase analyser. The pressure, temperature and resonant frequency of the QCM are recorded by a PC.
**Wax-Hydrate Visual Rig**

**Main applications:**

1. Measuring wax appearance and disappearance temperatures by visual and QCM techniques.
2. Measuring the hydrate stability zone of various fluid systems.
3. Investigating the mechanism of hydrate inhibition by low dosage hydrate inhibitors, using the visual capabilities of the rig.
4. Studying the effect of gas hydrates on wax and vice versa.
5. Measuring the interfacial tension of various fluid systems by pendant drop technique

**Operating conditions:**

Pressure: up to 7,500 psia (50 MPa)

Temperature: -30 °C to 80 °C

**Description:**

The Wax-Hydrate Visual Rig is comprised of a 100cc cell with a maximum operating pressure of 50 MPa. The ends of the cell are removable and are fitted with 4cm diameter sapphire windows giving good visibility of the entire contents of the cell. A jacket through which fluid can be circulated from a temperature controlled bath surrounds the cell, giving the Rig an operating temperature range of -30 to 80 °C. The cell is mounted on a compressed air powered rocking mechanism for mixing of contents. Cell pressure, temperature and QCM resonant frequency are recorded by a PC. A magnifying camera can be mounted on the rig, which is connected to a PC for digital image and video capture. The Rig is used for studying gas hydrates, wax and combinations of them.
Medium Pressure Micromodel

Main applications:
1. Visual observation of gas hydrate formation and dissociation in various fluid systems.
2. Simulating gas hydrate formation in porous media.
4. Effect of various chemicals (in particular Low Dosage Hydrate Inhibitors) on crystal growth and morphology.
5. Mechanism of gas hydrate formation (and inhibition) in various fluid systems.
7. Investigating the mechanism of gas hydrate dissociation and gas release from natural gas hydrate reservoirs.

Operating conditions:
Pressure: up to 1,200 psia (8 MPa)
Temperature: -20 ºC to 80 ºC

Description:
The model consists of a sealed pore structure etched onto a glass plate. Fluids can be pumped through the model using piston vessels. The whole set-up is submersed in a temperature-controlled bath to allow experiments to be performed under hydrate forming conditions. The model can operate at pressures up to 8 MPa. A digital magnifying camera is mounted above the model, and digital images or video feed are captured by a computer. Some examples of images taken from the model are shown below.
High Pressure Micromodel

Main applications:
1. Visual observation of gas hydrate formation and dissociation in various fluid systems.
2. Simulating gas hydrate formation in porous media.
4. Effect of various chemicals (in particular Low Dosage Hydrate Inhibitors) on crystal growth and morphology.
5. Mechanism of gas hydrate formation (and inhibition) in various fluid systems.
7. Investigating the mechanism of gas hydrate dissociation and gas release from natural gas hydrate reservoirs.

Operating conditions:
Pressure: up to 6,000 psia (40 MPa)
Temperature: -20 °C to 80 °C

Description:
The heart of the micromodel facility consists of two glass plates, one has an etched micromodel that can be specifically designed geometrical networks such as pores and tubes or reproductions of actual thin sections of real sediments, the other is a plain cover plate. The cover plate has an inlet and outlet which allows fluids to be pumped through the enclosed pore network. Temperature is measured by a probe and can be kept stable to within 0.05°C. Pressure is monitored by means of a Quartzdyne pressure transducer (accurate to 0.007MPa). A digital magnifying camera is used to make video footages and take photographs of the glass micromodel during hydrate formation and dissociation and this is stored by PC.
Porous Media Rig

Main applications:

1. Measuring the effect of pore size, saturation and wettability on gas hydrate stability zone in porous media.
2. Investigating the kinetics of gas hydrate formation and dissociation in porous media.
3. Effect of pore water salinity on the hydrate stability zone.

Operating conditions:

Pressure: 6,000 psia (40 MPa)
Temperature: -20 °C to 80 °C

Description:

The rig consists of a small-volume, high pressure cell, capable of operating up to 40 MPa. Pressure is monitored by a quartzdyne pressure transducer with an accuracy of 0.007 MPa. Temperature is controlled by circulating coolant around a cell jacket, and is monitored by a PRT with an accuracy of 0.01 °C. Temperature cycles and the collection of data is controlled by an automated computer system.
Main applications:

1. Detecting and quantifying gas hydrates in sediments by physical techniques
2. Effect of sediment mineralogy and/or over burden pressure on the phase behaviour of gas hydrates in sediments.
3. Simulating various formation and dissociation scenarios for natural gas hydrates.
4. Simulating various gas production techniques from natural gas hydrates.
5. Investigating the effect of LDHIs on gas hydrate formation and inhibition.
6. Measuring acoustic properties of various fluid systems.
7. Measuring saturation pressure using ultrasonic techniques.

Operating conditions:

Pressure: up to 6,000 psia (40 MPa)
Temperature: -20 ºC to 80 ºC

Description:

The Ultrasonic Rig consists of a stainless steel cell which is filled with real or artificial unconsolidated sediments or consolidated rock cores. The cell is surrounded by a coolant jacket with circulating fluids controlled by a programmable cryostat (-20 to 80 ºC) and is stable to within 0.05 ºC. The system has a maximum operating pressure of 41 MPa. Sediment overburden and pore fluid pressures can be controlled independently. Temperature and pressures are monitored by means of a PRT and Quartzdyne pressure transducers (accuracy of 0.01 MPa), respectively. At the two ends of the cell, an ultrasonic transmitting transducer and a receiving transducer are mounted in each end cap. Transducers can be compressional or shear, or combinations of P-wave and S-wave at a central frequency of 1 MHz. An ultrasonic pulser/receiver (P/R) is connected to the two transducers to generate and receive pulse signals. The received signal through test sediments is amplified by the P/R and the sent to a digital storage oscilloscope (DSO). The DSO acquires the series of pulse waves and sends data to a personal computer (PC) through a parallel port interface. The PC shows waveforms on its screens and saves data in both waveform and data format for further processing.
This rig is an advanced version of the Ultrasonic rig-1. The 60 cm long rig has:

1. The ability to establish a temperature gradient along its length.
2. Thermocouples along the length for measuring temperature
3. Resistivity measurement capabilities along its length
4. Ability to rotate 0-90º

The rig has almost all the capabilities of Ultrasonic Rig-1. With respect to studying gas hydrates in sediments, the rig has many extra capabilities.
This rig can be used as a high pressure glass micromodel (very much similar to the previous rig) with similar capabilities. However, it is possible to change the cap and use it as a kinetic rig with visual capabilities (through two windows), ultrasonic pluser and receiver and Quartz Crystal Microbalance (QCM) set-up for detecting solid (hydrate, wax, etc) formation and deposition.

**Operating conditions:**
Pressure: up to 6,000 psia (40 MPa)
Temperature: -20 °C to 80 °C
**Other Supporting Equipments:**

1. Freezing point measurement equipment
2. Boiling point measuring rig.
3. Solubility and salting-out measurement rig.
4. ASTM Cloud point determination set-up
5. GC and GC/MS facilities
6. Gas meter
7. High accuracy Quixiz pumps

The above equipment are housed in two modern and purposed built laboratories.

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**Notes:**

In most cases the temperature limitations mentioned for each rig can be extended by minor modifications to the rig and/or cooling/heating systems.

The above list is intended to provide an indication of the capabilities of each experimental set-up. However, these capabilities could be used for other applications where required.

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APPENDIX B

Pressure and Temperature Profiles of the Tests in the Kinetic Rigs
Figure 1. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 4.3 °C and 100 bar, rpm=600

Figure 2. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 4.3 °C and 100 bar, rpm=600
Figure 3. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 4.9 °C and 100 bar, rpm=600

Figure 4. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 4.9 °C and 100 bar, rpm=600
Figure 5. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 5.3 °C and 100 bar, rpm=600

Figure 6. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 5.3 °C and 100 bar, rpm=600
Figure 7. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 6 °C and 100 bar, rpm=600

Figure 8. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 6.7 °C and 101 bar, rpm=600
Figure 9. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 7.4 °C and 101.4 bar, rpm=600

Figure 10. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 7.5 °C and 101.5 bar, rpm=600
Figure 11. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 7.6 °C and 101.4 bar, rpm=600.

Figure 12. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 4.3 °C and 100 bar, no mixing.
Figure 13. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 4.9 °C and 100 bar, no mixing.

Figure 14. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 7.1 °C and 101 bar, no mixing.
Figure 15. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 7.3 °C and 101 bar, no mixing.

Figure 16. Pressure and temperature profiles for NG-water –5vol% HYTREAT® 04-049. Testing conditions: 7.3 °C and 101 bar, no mixing.
Figure 17. Pressure and temperature profiles for NG-water–0.5 mass% PVCap. Testing conditions: 4.5 °C and 100 bar, rpm=600.

Figure 18. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.5 mass% PGPE. Testing conditions: 4.4 °C and 100 bar, rpm=600.
Figure 19. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.75 mass% PGPE. Testing conditions: 4.4 °C and 98 bar, rpm=600.

Figure 20. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.75 mass% PGPE. Testing conditions: 4.3 °C and 98 bar, rpm=600.
Figure 21. Pressure and temperature profiles for NG-water–0.5 mass% PVCap. Testing conditions: 4.6 °C and 100bar, rpm=600.

Figure 22. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.5 mass% PGPE. Testing conditions: 4.6 °C and 100bar, rpm=600.
Figure 23. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.75 mass% PGPE. Testing conditions: 4.5 °C and 98 bar, rpm=600.

Figure 24. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.75 mass% PGPE. Testing conditions: 4.8 °C and 100 bar, rpm=600.
Figure 25. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.75 mass% PGPE. Testing conditions: 4.8 °C and 100 bar, rpm=600.

Figure 26. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.75 mass% PGPE. Testing conditions: 4.9 °C and 100 bar, rpm=600.
Figure 27. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.75 mass% PGPE. Testing conditions: 4.9 °C and 100 bar, rpm=600.

Figure 28. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.75 mass% PGPE. Testing conditions: 4.4 °C and 100 bar, no mixing.
Figure 29. Pressure and temperature profiles for NG-water–0.5 mass% PVCap-0.75 mass% PGPE. Testing conditions: 4.3 °C and 100 bar, no mixing.

Figure 30. Pressure and temperature profiles for NG-water–0.5 mass% PVCap. Testing conditions: 5.0 °C and 100 bar, no mixing.
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 31. Pressure and temperature profiles for NG-water–0.5 mass% PVCap. Testing conditions: 4.8 °C and 100 bar, no mixing.

Figure 32. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Corrtreat 799. Testing conditions: 4.4 °C and 70.5 bar, rpm=1000
Figure 33. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Corrtreat 799. Testing conditions: 5°C and 72 bar, rpm=1000.

Figure 34. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Corrtreat 799. Testing conditions: 5.3 °C and 71 bar, rpm=1000.
Figure 35. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Corrtreat 799. Testing conditions: 5.3 °C and 73 bar, rpm=1000.

Figure 36. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Corrtreat 799. Testing conditions: 6 °C and 71.5 bar, rpm=1000.
Figure 37. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Corrtreat 799. Testing conditions: 5.9°C and 70 bar, rpm=1000.

Figure 38. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Corrtreat 799. Testing conditions: 5.2 °C and 71 bar, no mixing.
Figure 39. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Cortreat 799. Testing conditions: 5.2 °C and 71 bar, no mixing.

Figure 40. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Cortreat 799. Testing conditions: 6.3 °C and 71 bar, no mixing.
Figure 41. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Corrtreat 799. Testing conditions: 6.2 °C and 71 bar, no mixing.

Figure 42. Pressure and temperature profiles for NG-water –1 mass% PVCap and 500ppm Corrtreat 799. Testing conditions: 7 °C and 70.7 bar, no mixing.
Figure 43. Pressure and temperature profiles for NG-water –1 mass% PVCap. Testing conditions: 5 °C and 73 bar, rpm=1000.

Figure 44. Pressure and temperature profiles for NG-water –1 mass% PVCap. Testing conditions: 4.8 °C and 73 bar, rpm=1000.
Figure 45. Pressure, temperature and torque profiles for Condensate (LTB98-1-C) NG-water, rpm=400.

Figure 46. Pressure, temperature and torque profiles for Condensate (LTB98-1-C) NG-water and 2.5 vol% HT03-186, rpm=400.