FLOW ASSURANCE:

MICRO AND MACRO-SCALE EVALUATION OF LOW DOSAGE HYDRATE INHIBITORS

2002 – 2005 PROGRAMME

PROGRESS REPORT
December 2004 – May 2005
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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
- 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
- APPENDIX C: SUMMARY OF SYNERGISTS DESCRIBED IN PATENTS ........................... C.1
PERSONNEL AND SPONSORS

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, BP, 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 hydrate in the presence of 1 mass% PVCap with and without carrier fluid were compared. While the result of the test with carrier fluid shows that the hydrate crystals mainly exhibit continuous solid hydrate crystals, the test without carrier fluid exhibits thin patches of hydrate crystals. This suggests that the carrier fluid has some effect on the morphology of hydrate crystals at these conditions.
- The synergistic effect of Propylene Glycol Propyl Ether (PGPE) on PVCap polymers with different lengths/molecular weights was studied. The results show that there is a marked improvement in inhibitor performance in the presence of PGPE in longer polymers.
- The inhibition effect of the combination of the BASF advanced polymer and PVCap in natural gas system at different degrees of subcooling was tested. The results showed that the inhibition effect of a mixture of 0.5 mass% PVCap and 2.5 volume% BASF advanced polymer is better than that of 5 volume% of BASF advanced polymer.
- The role of polymer carrier fluids on hydrate inhibition was studied. The results of the experiments showed that 1.5 mass% ethylene glycol as carrier fluid slightly decreases the inhibition effect of PVCap.
- The inhibition effect of PVCap in natural gas-water system at subzero conditions was investigated. In order to prevent ice formation, and provide a similar degree of subcooling at the same pressure range (but at a different temperature) ethylene glycol (20 mass%) was added to water. The tests results showed that PVCap in
the presence of 20 % ethylene glycol can inhibit hydrate formation at subzero conditions. Furthermore, 20 mass% ethylene glycol has a positive effect on the performance of PVCap.

- The performance of a new anti-agglomerant (HT04-106) was tested in a kinetic rig equipped with a helical tube mixer by means of torque measurement. The results of the tests showed the applicability of the method and good performance of the anti-agglomerant.

- The nucleation and growth of hydrate in the presence of PVCap (without solvent) in natural gas water system at static conditions was investigated in an ultrasonic set up. By comparison to the previous test with LUVICAP®, the tests results suggest that the presence of ethylene glycol as a carrier fluid in LUVICAP® would allow more hydrates growing into the liquid phase, however it would not significantly affect the induction time of PVCap-natural gas-water system.

- The test results on the combination of PVCap with BASF advanced polymer in natural gas-water system conducted in the ultrasonic rig showed that, at static conditions, addition of BASF advanced polymer to LUVICAP® could improve the performance of PVCap to some extent.

- The dependence of synergistic effect of glycol ether compounds on their molecular structures was investigated in ultra-sonic set-up. Propylene Glycol Propyl Ether (PGPE) and two other glycol ether compounds, Ethylene Glycol Monobutyl Ether (EGME) and Ethylene Glycol Diethyl Ether (EGDE), were examined. The three glycol ether compounds have an identical molecular formula but different molecular structures. The results of the experiments showed that PGPE, which has a non-linear molecular structure and a secondary hydroxyl, achieved significantly longer nucleation time than the other two glycol ethers that have a linear molecular structures.
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 rigs to investigate: a) the effect of the synergist Propylene Glycol Propyl Ether on the hydrate inhibition performance of different lengths of PVCap, b) the inhibition effect of the combination of two kinetic hydrate inhibitors; BASF advanced polymer and PVCap in natural gas–water system in bulk conditions, c) the role of polymer carrier fluid in hydrate inhibition, d) the inhibition effect of PVCap in natural gas-water system at subzero conditions, and e) the performance of a new anti-agglomerant (HT04-106) in a natural gas-water-condensate system by the means of measuring torque in a kinetic rig equipped with a helical tube mixer. The hydrate pattern growth and plugging in the presence of a PVCap base polymer was investigated by visual observation in the high-pressure micromodel rig. The effect of a corrosion inhibitor on the performance of the kinetic hydrate inhibitor under both static and flowing conditions was also investigated by visual observation in the high pressure micromodel rig. A high-pressure windowed rig was used for visualisation of hydrate growth patterns in a natural gas system in the presence of a pure PVCAP polymer. Nucleation tests in the ultrasonic rig have been carried out with dried LUVICAP® to examine the effect of ethylene glycol as a carrier fluid on hydrate inhibition. The
effect of molecular structure of synergistic chemicals on the performance of PVCap was investigated by experiments carried out in the ultrasonic rig.

**Micromodel Experiments**

The experimental studies were carried out to visually observe the hydrate growth patterns and plugging in the presence of a PVCap base polymer. The experiments were conducted in a natural gas-water system with 1 mass% PVCap base polymer at 109 bar under both flowing and static conditions. As expected, the presence of PVCap would slow down hydrate growth, delay blockage and also prevent hydrate formation in the water phase as compared to the blank test without inhibitor (a summary of the results is presented in Table 1). Hydrate deposits appeared to be more porous with the formation of patches of hydrate crystals, both at flowing and static conditions as shown in Figure 1.

<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>
<th>Comments (growth &amp; crystals morphology, etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>13.7</td>
<td>4.8</td>
<td>0.7</td>
<td>85</td>
<td>Continuous solid and non-porous hydrate crystals in both phases</td>
</tr>
<tr>
<td>Pure PVCap</td>
<td>13.7</td>
<td>4.8</td>
<td>20 *</td>
<td>-</td>
<td>* Initial slow growth</td>
</tr>
<tr>
<td>Pure PVCap at static conditions</td>
<td>2.0</td>
<td>16.5</td>
<td>0</td>
<td>40</td>
<td>Catastrophic growth in gas phase; patches of hydrate crystals in gas phase</td>
</tr>
<tr>
<td>Pure PVCap at static conditions</td>
<td>3.0</td>
<td>15.5</td>
<td>-</td>
<td>N/A</td>
<td>Patches of hydrate crystals in gas phase</td>
</tr>
<tr>
<td>PVCap (in LUVICAP® + Ethylene glycol)</td>
<td>4.5</td>
<td>14</td>
<td>-</td>
<td>N/A</td>
<td>Continuous solid hydrate crystals in gas phase</td>
</tr>
</tbody>
</table>

---

![Image of hydrate deposits]

*0.5 mm*

---

**Table 1: Summary of Results: dried PVCap base polymer at 109 bar**
The natural gas hydrate crystals growth in the presence of 1 mass% PVCap with and without carrier fluid were compared. While the result of the test with carrier fluid shows that the hydrate crystals mainly exhibit continuous solid hydrate crystals, the test without carrier fluid exhibits thin patches of hydrate crystals (Figure 2). This suggests that the carrier fluid has some effect on the morphology of hydrate crystals at these test conditions.

Figure 1. Images of hydrate deposits for Natural Gas – Water system under flowing condition at 109 bar with (a) blank test (4.8°C subcooling), (b) 1 mass% PVCap (16.5°C subcooling)

Figure 2. Comparison of hydrate morphology for Natural Gas – Water system in the presence of 1 mass% PVCap (a) with carrier fluid (14 °C subcooling) (b) without carrier fluid (15.5 °C subcooling)

The effect of the corrosion inhibitor (500 ppm Corrtreat 799) on the performance of the kinetic hydrate inhibitor (1.25 mass% LUVICAP®) under both static and flowing conditions was investigated. The summary of results is presented in Table 2. Based on these preliminary experiments, the results suggest that the presence of corrosion inhibitor has an adverse effect on the performance of PVCap. This was observed from the fact that catastrophic hydrate formation began at 11 °C subcooling in the presence of corrosion inhibitor, while in the absence of CI, the catastrophic hydrate growth began at 13 °C subcooling. In addition, it was observed that hydrate formed both in water and gas phase in the presence of corrosion inhibitor as shown in Figure 3. This suggest that PVCap failed to prevent hydrate formation in the water phase in the presence of corrosion inhibitor.
Table 2: Summary of Results: Effect of corrosion inhibitor at 109 bar

<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>
<th>Comments (growth &amp; crystals morphology, etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUVICAP®</td>
<td>8</td>
<td>11</td>
<td>4 *</td>
<td>-</td>
<td>* Initial slow growth</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>13</td>
<td>1.23</td>
<td>13.6</td>
<td>Catastrophic growth of hydrate; non porous solid hydrate in gas phase</td>
</tr>
<tr>
<td>LUVICAP® + CI</td>
<td>8</td>
<td>11</td>
<td>1.8</td>
<td>-</td>
<td>Catastrophic growth of hydrate; small gas bubbles present; ΔP fluctuate</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>13</td>
<td>0</td>
<td>-</td>
<td>Catastrophic growth of hydrate; increase in ΔP due to hydrate build-up; terminate test at 4°C</td>
</tr>
<tr>
<td>LUVICAP® + CI</td>
<td>6</td>
<td>13</td>
<td>3</td>
<td>~ 47</td>
<td>Catastrophic growth of hydrate; hydrate formed in both phases</td>
</tr>
<tr>
<td>LUVICAP® + CI at static condition</td>
<td>4</td>
<td>14.5</td>
<td>0</td>
<td>N/A</td>
<td>Thin deposit of hydrate crystals in both phases</td>
</tr>
</tbody>
</table>

(a) without corrosion inhibitor  (b) with corrosion inhibitor

Figure 3. Comparison of hydrate morphology for Natural Gas – Water system in the presence of 0.5 mass% PVCap at 13 °C subcooling (a) without corrosion inhibitor (b) with 500 ppm Corrosion Inhibitor.

**Kinetics Rig Experiments**

Five series of experiments were conducted using the kinetic rigs. In the first series of experiments the synergistic effect of Propylene Glycol Propyl Ether (PGPE) on PVCap polymers with different lengths/molecular weights was studied. A previous study into the synergy phenomenon proposes that the synergistic chemicals improve the performance of the inhibitors by altering their conformation in solution. It is
proposed that these synergistic chemicals alter the shape of the polymers of different lengths in different ways. Tests were carried out to investigate the effect that the synergist (PGPE) had on the hydrate inhibition performance of different lengths of PVCap. The polymers used were supplied by BASF and are described below:

- **LUVICAP®** (2000-8000 Daltons, dry polymer)
- **LUVISKOL®** (~100,000 Daltons, 40% active polymer based in ethanol)
- **LUBASIN®** (~1,000,000 Daltons, 40% active polymer based in ethanol).

It was required to remove the above polymers from their commercial solvents to attain a dry polymer (LUVISKOL®, LUBASIN®). The polymers were separated via drying. LUVICAP® was supplied dry, and thus there was no requirement for separation. A concentration of 1 mass% active polymer with concentrations of 0%, 0.75% of (PGPE), was made up with distilled water for the three polymers. Tests were conducted for the various inhibitors, and inhibitor plus synergist solutions to determine the maximum subcooling that the specified inhibitor solutions could delay the onset of hydrate growth and nucleation. In Table 3 the summary of the tests results is shown, with the emphasis based on the temperature at which the induction time almost disappears i.e. less than 120 minutes. This value of subcooling taken is the arithmetic average between a point of “no induction” ($t_i<2$ hours), and a point where there is a significant induction time ($t_i>2$ hours). The results show that there is a marked improvement in inhibitor performance in the presence of 0.75% PGPE in both of the longer polymers, at 10.6% and 8.4% for LUVISKOL® and LUBASIN® respectively. There was a negligible improvement of 3.8% for the shorter LUVICAP® polymer in the presence of 0.75% PGPE. This follows the theory that the synergists enable the larger polymers to unwind to a larger extent.

<table>
<thead>
<tr>
<th>Level of subcooling where no induction time present</th>
<th>% difference in performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% PGPE</td>
<td></td>
</tr>
<tr>
<td>LUVICAP® 10.5°C</td>
<td>-</td>
</tr>
<tr>
<td>0.75% PGPE 10.9°C</td>
<td>3.8%</td>
</tr>
<tr>
<td>1.5% PGPE 10.5°C</td>
<td>-3.7%</td>
</tr>
<tr>
<td>LUVISKOL 10.4°C</td>
<td>-</td>
</tr>
<tr>
<td>0.75% PGPE 11.5°C</td>
<td>10.6%</td>
</tr>
<tr>
<td>1.5% PGPE -</td>
<td>-</td>
</tr>
<tr>
<td>LUBASIN® 8.3°C</td>
<td>-</td>
</tr>
<tr>
<td>0.75% PGPE 9.0°C</td>
<td>8.4%</td>
</tr>
<tr>
<td>1.5% PGPE -</td>
<td>-</td>
</tr>
</tbody>
</table>
In the presence of 1.5% PGPE the performance of LUVICAP® was reduced by 3.7%. This follows the notion of an optimum inhibitor concentration; which may have already been passed (Cohen et al., 1998). This data suggests that too much of a solvent or synergist may become an antagonist to the inhibitors.

In the second series of experiments in kinetic rigs the inhibition effect of the combination of the BASF advanced polymer and PVCap in natural gas system at different degrees of subcooling was tested. The results of the experiments have been summarised in Table 4. As seen in Table 4, in the presence of 0.5 mass% PVCap at 13.2 °C subcooling the induction time is about 3-5 hours (Tests No.1-2). Addition of 2.5 volume percent of HYTREAT® 04-049 to the system at similar conditions (13.3 °C subcooling) extended the induction time to 13-14 hours (Tests No.3-4) and at higher degrees of subcooling (13.7 °C) 9-11 hours induction time achieved by the combination of inhibitors (Tests No.5-6). Comparing the test results with previous tests results on 5 volume percent of HYTREAT® 04-049 at similar conditions, it seems that for the above mentioned test conditions, the hydrate inhibition effect of a mixture of 0.5 mass% PVCap and 2.5 volume% of HYTREAT® 04-049 is better than that of 5 volume% of HYTREAT® 04-049.

Table 4. Experimental results obtained from the Kinetic Rig 2 for PVCap and the mixture of PVCap and (HYTREAT04-049) solution in the presence of natural gas at 600 rpm mixing rate.

<table>
<thead>
<tr>
<th>Test No</th>
<th>PVCap mass%</th>
<th>HYTREAT® (04-049) vol%</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>0.5</td>
<td>0</td>
<td>5.5 / 102</td>
<td>13.2</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0</td>
<td>5.5 / 102</td>
<td>13.2</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>2.5</td>
<td>5.3 / 101</td>
<td>13.3</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>2.5</td>
<td>5.3 / 101</td>
<td>13.3</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>2.5</td>
<td>4.8 / 100</td>
<td>13.7</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>2.5</td>
<td>4.8 / 100</td>
<td>13.7</td>
<td>9</td>
</tr>
</tbody>
</table>

The third series of experiments were conducted to investigate the role of polymer carrier fluids on hydrate inhibition. The experiments were carried out with a natural gas-water system in the presence of pure PVCap (dried LUVICAP®) and LUVICAP® (PVCap and ethylene glycol), both at similar conditions. For comparison the pressure profiles of the tests have been shown in Figure 4. As shown in Figure 4, after 20 hours, the rate of growth in the presence of 1.5 mass% ethylene glycol is higher as compared to the tests with pure PVCap. It seems that in the conditions the
experiments carried out ethylene glycol slightly decreases the inhibition effect of PVCap.

Onshore pipelines could be subjected to subzero conditions where in the presence of natural gas and water, thermodynamic and/or kinetic hydrate inhibitors are needed to prevent hydrate formation. The fourth series of tests conducted in the kinetic rigs were designed to evaluate the inhibition effect of PVCap in natural gas-water systems at subzero conditions. In order to prevent ice formation, and provide a similar degree of subcooling at the same pressure range, but at a different temperature, ethylene glycol (20 mass%) was added to water. The pressure profiles of the tests at 13.4 °C and 15 °C subcooling are shown in Figure 5.

Figure 4. Pressure profiles of the experiments in natural gas system in the presence of pure PVCap and LUVICAP® (PVCap and ethylene glycol).

It seems that for natural gas-water system, 1 mass% PVCap in the presence of 20 mass% ethylene glycol can inhibit hydrate formation at subzero conditions. For comparison two tests were conducted in a natural gas-water system in the presence of 2.5 mass% LUVICAP® (1 mass% PVCap and 1.5 mass% EG) at a similar pressure and degree of subcooling (13.3 °C). The pressure and temperature profiles of one the tests have been shown in Figure 5. As shown in the figure, at similar degrees of subcooling (13.3-13.4 °C), in the presence of 20 mass% EG, a longer induction time
and a lower rate of growth are observed in comparison to 1.5 mass% EG. Similar pressure profiles were observed by increasing the subcooling to 15 °C. While further tests are needed, the preliminary results shows that 20 mass% ethylene glycol has a positive effect on the performance of PVCap.

The fifth series of experiments was carried out in a kinetic rig equipped with a helical tube mixer for evaluating the performance of a new anti-agglomerant (labelled as HT04-106 and provided by Clariant Oil Services) in a natural gas-water-condensate system by means of torque measurement. A total of four experiments were conducted in a kinetic rig with a mixing rate of 400 rpm. A solution of 33 volume % water in condensate was used in the tests, in the presence and absence of an anti-agglomerant (HT04-106). The pressure, temperature and torque profiles of the experiments in the absence and presence of AA are presented in Figures 6 and 7 respectively.

![Figure 5. Pressure profiles of the experiments in natural gas-1 mass% PVCap in water system at temperatures above and below zero °C.](image)

Figure 5. Pressure profiles of the experiments in natural gas-1 mass% PVCap in water system at temperatures above and below zero °C.
Figure 6. Pressure, temperature and torque profiles for Condensate-NG-water system, kinetic rig 5, helical mixer, rpm=400.

Figure 7. Pressure, temperature and torque profiles for NG-Condensate-Water system in the presence of 0.5 mass% AA (HT04-106) in water phase. W/C=0.33, Kinetic Rig 5, helical tube mixer, rpm=400.

By comparing the torque profiles for the experiments (Figures 6-7), it can be seen that
after hydrate formation in both cases, the same maximum torque is observed, however in the test with anti-agglomerant the stabilised torque (41) after hydrate formation is much less than that of blank test (106) denoting the transportability of the hydrate slurry.

**Experimental Measurements Made Using High Pressure Visual Rig**

**Hydrate growth patterns**
Tests were conducted in a high pressure visual cell in order to observe the growth pattern of natural gas hydrates in the presence of an aqueous solution of PVCap polymer. In previous work, tests were carried out with an aqueous solution comprised of 2.5 mass% LUVICAP® and the growth pattern of natural gas hydrates was found to be very different from that when distilled water was present. It was decided to investigate the effect of the different components that make up an aqueous solution of 2.5 mass% LUVICAP®, these being ethylene glycol (1.5 mass%) and PVCap polymer (1 mass%). The effect of an aqueous solution comprised of 1.5 mass% ethylene glycol was presented at the previous steering committee meeting leaving the effect of 1 mass% PVCap polymer to complete the picture. Figure 8 shows the pressure and time data for the test with an aqueous solution of PVCap polymer compared to the previous data from tests with LUVICAP® and ethylene glycol. This indicates that there were differences from a kinetic point of view between the systems. Only in the test with LUVICAP® was there no induction time. In the test with ethylene glycol the initial formation rate was higher than for the other two tests. The hydrate growth rate in terms of pressure reduction with time was similar for the tests with polymer present.

The growth pattern, from a visual point of view, was similar for the tests with polymer present, hydrate formation beginning at the gas/water interface and on the walls in the upper part of the test cell. Water was drawn from the lower part of the cell and most of the hydrates were seen to form mainly in the upper part of the cell. In the test with the PVCap polymer alone, the hydrates appeared grainy and the layer of hydrates that had initially formed at the gas/water interface broke up leaving a conical looking pieces of hydrate. Figure 9 shows the start of hydrate formation in the test with
PVCap polymer, Figure 10 shows the grainy appearance of the hydrates and Figure 11 shows the pieces of hydrate remaining after the original hydrate layer was broken up.

**Interfacial tension measurements**

The high pressure visual rig was also used to make interfacial tension (IFT) measurements. Measurements were made of the IFT between liquid water and vapour phases in the systems methane with an aqueous solution of HYTREAT® 04-049 (BASF advanced polymer based KHI) and methane with an aqueous solution of HYTREAT® 03-187 (PVCap based KHI). Figure 12 shows the experimental data along with previously measured data for methane and distilled water and methane with an aqueous solution of LUVICAP®.

![Figure 8. Pressure and time data for tests with natural gas in the presence of 1 mass% PVCap polymer, natural gas in the presence of 1.5 mass% ethylene glycol, and natural gas in the presence of 2.5 mass% LUVICAP®.](image-url)
Figure 9. Picture showing the start of natural gas hydrate formation at the gas/water interface in the test with natural gas and an aqueous solution comprised of 1 mass% PVCap polymer.

Figure 10. Picture showing the grainy appearance of the natural gas hydrates formed in the test with natural gas and an aqueous solution comprised of 1 mass% PVCap polymer.
Figure 11. Picture showing the pieces of hydrate left after the break up of the solid layer originally formed at the gas/water interface in the test with natural gas and an aqueous solution comprised of 1 mass% PVCap polymer.

Figure 12. Summary of experimental IFT data between methane and distilled water and methane and different aqueous solutions of hydrate inhibitors.

**Hydrate Nucleation Tests Using Ultrasonic Waves**

In the last six months further nucleation tests have been conducted to investigate the effect of ethylene glycol as a carrier fluid in LUVICAP®, the performance of the combination of PVCap with BASF Advanced Polymer, and the effect that molecular structures of glycol ethers have on the performance of PVCap. In the tests on synergistic chemicals, in addition to Propylene Glycol Propyl Ether (PGPE) that was
tested before, two other glycol ether compounds, Ethylene Glycol Monobutyl Ether (EGME) and Ethylene Glycol Diethyl Ether (EGDE), were examined. The three glycol ether compounds have an identical molecular formula but different molecular structures.

The test with the dried version of LUVICAP® showed that there was almost no further pressure decrease and FFT and amplitude drop after the system temperature reached the target temperature. By comparison to the previous test with LUVICAP® (40 mass% of PVCap and 60 mass% of ethylene glycol), where the FFT and amplitude dramatically dropped and the system pressure continuously decreased although the system temperature had been stable, it may suggest that, at static conditions, the presence of ethylene glycol as a carrier fluid in LUVICAP® would allow more hydrates growing into the liquid phase. However, the result also showed that the presence of ethylene glycol would not significantly affect the induction time of PVCap-water system.

The test results on the combination of PVCap with BASF Advanced Polymer showed that, at static conditions, addition of HYDREAT04-049 to LUVICAP® could improve the performance of PVCap to some extent. For example, as can been seen in Figure 13, by adding 2.5 vol% of BASF Advanced Polymer (HYDREAT04-049) to 0.5 mass% of PVCap (1.25 mass% of LUVICAP®), the nucleation time is 4.7 hours; the delay of catastrophic growth is about 19 hours, compared to a nucleation time of 1 hour and a catastrophic growth delay of about 5 hours in the previous test with 0.5 mass% of PVCap alone, shown in Figure 14.

(a) The profile of the system temperature, pressure, and the ultrasonic signals.
(b) Responses of the ultrasonic signals to hydrate nucleation in details.

Figure 13. Hydrate nucleation and growth in the presence of 0.5 mass% PVCap plus 2.5 vol% of HYDREAT04-049 (Legend: P=Pressure, T=Temperature, A=Amplitude).

Figure 14. Hydrate nucleation and growth in the presence of 0.5 mass% PVCap.

Table 5 summarises the results of the glycol ether tests to investigate the dependence of synergistic effect of glycol ether compounds on their molecular structures. At static conditions, the test with 0.5 mass% of PVCap plus 0.75 mass% of PGPE, which has a non-linear molecular structure and a secondary hydroxyl, gave significantly longer nucleation time (6.6 hours) and delayed the catastrophic growth for more than 48 hours, and also effectively prevented hydrates growing into liquid phase. In the other tests with either EGME or EGDE that have a linear molecular structure, no significant difference between the nucleation times could be observed, even if EGME has a primary hydroxyl. However, it is clear that the addition of glycol ether compounds as synergists can significantly delay the catastrophic growth in the PVCap-water systems.
<table>
<thead>
<tr>
<th>Glycol ether compounds</th>
<th>Nucleation time /hour</th>
<th>Delay of catastrophic growth /hour</th>
<th>Hydrate quantity in liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGPE</td>
<td>6.6</td>
<td>&gt; 48</td>
<td>Little</td>
</tr>
<tr>
<td>EGME</td>
<td>1.5</td>
<td>30</td>
<td>Large quantity</td>
</tr>
<tr>
<td>EGDE</td>
<td>1.5</td>
<td>&gt;70</td>
<td>Some</td>
</tr>
<tr>
<td>None</td>
<td>1</td>
<td>5</td>
<td>Large quantity</td>
</tr>
</tbody>
</table>
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-streams 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 practices; 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 processes, 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 hydrate stability zone. 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
Chapter 1 Introduction

- 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 with visual capabilities
- Two ultrasonic rigs (400 bar)
- 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 3 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 (Bringdal, 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 corrosion inhibitors and/or other chemicals, and/or gas composition, and/or presence of a liquid hydrocarbon phase. 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, several experiments were carried out in the high pressure micromodel set up to investigate the hydrate pattern growth and plugging characteristics in the presence of PVCap base polymer and the effect of the corrosion inhibitor on the performance of the kinetic hydrate inhibitor under both static and flowing conditions. Chapter 2 presents the details of the experiments conducted in micromodel set-up.

Chapter 3 presents the results of the experiments carried out on in the kinetic rigs. The experiments were carried out in the kinetic rigs to investigate: a) the effect of the synergist Propylene Glycol Propyl Ether on the hydrate inhibition performance of different lengths of PVCap, b) the inhibition effect of the combination of two kinetic hydrate inhibitors; BASF advanced polymer and PVCap in natural gas –water system in bulk conditions, c) the role of polymer carrier fluid in hydrate inhibition, d) the inhibition effect of PVCap in natural gas-water system below the ice point, and e) the performance of a new anti-agglomerant (HT04-106) in a natural gas-water-condensate system by the means of measuring torque in a kinetic rig equipped with a helical tube mixer.

Visual observation of hydrate formation in the presence and absence of LDHI in bulk conditions proved very helpful in understanding the reasons for the failure of KHI under static conditions. The experimental set-up was equipped with a Pendant Drop IFT measurement device to examine the role of LDHIs in changing the system’s IFT and its relation with the performance LDHIs. Visual observations of hydrate formation in natural gas-water in the presence of pure PVCAP polymer at bulk conditions are presented in Chapter 4.

For the first time ultrasonic waves were used to identify the various stages in gas hydrate nucleation and growth. The results so far have been very promising and a patent has been filed. Chapter 5 describes the results of the tests in ultrasonic set up carried out to investigate the effect of molecular structure of synergistic chemicals on the performance of PVCap.
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 phase of project, the experiments for natural gas-water system with 5 volume% of a new kinetic inhibitor (labelled as HYTREAT 04-049 and containing 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). Characteristic behaviour of hydrate plugging in the presence and absence of LDHI and/or synergist at simulated pipeline conditions was investigated under flowing conditions.

During the last meeting, the results of experiments carried out using visual cell suggested that the carrier fluid may mask the basic properties of the polymer used as Kinetic Hydrate Inhibitor (KHI). Therefore, studies were carried out within the last six months to investigate hydrate growth patterns and plugging in the presence of pure PVCap without carrier fluid using micromodel set-up and the new visual kinetic rig. The study on the compatibility of the corrosion inhibitor with PVCap demonstrated that the corrosion inhibitor has negative impact on the performance of PVCap. Further examination was suggested using micromodel set-up to study this effect. A series of tests was also proposed to investigate the hydrate particles size, distribution and plugging characteristics in the absence and presence of a new anti-agglomerate with 3 mass% NaCl in a water-condensate-natural gas system.

As detailed below, the experiments are divided into three parts to address the above-mentioned issues. The first part is to investigate the characteristic behaviour of hydrate plugging and hydrate growth pattern in the presence of 1.0 mass% of PVCap base polymer on natural gas-water system under flowing and static conditions using multi-channel flow conduit. The second part of the experiment is focused on studying the effect of corrosion inhibitor (CI) on the performance of KHI using similar system as in the first part. The third part is investigating the hydrate crystal particles size, the
distribution of phases and the characteristic of plugging in the presence of a new anti-
agglomerant with 3 mass% NaCl both under flowing and shut in conditions. The
latter experiments are in progress and the results will be presented during the Steering
Committee Meeting.

2.2. EXPERIMENTAL PROCEDURE
A multichannel flow conduit glass micromodel shown in Figure 2.1 was used in the
experiments on the PVCap base polymer and corrosion inhibitor. Tests were
conducted under flowing and static conditions for natural gas-water system in the
presence of 1.0 mass% pure polyvinylcaprolactam (PVCap) supplied by BASF. The
natural gas (composition listed in Table 1) supplied by Air products was used for this
study. For testing the effect of corrosion inhibitor, 0.5 mass % of PVCap (1.25
mass% LUVICAP®) was mixed with 500 ppm of corrosion inhibitor (labelled as
Corrtreat 799 and provided by Clariant Oil Services.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole%</th>
<th>Component</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>2.673</td>
<td>i-C₄</td>
<td>0.182</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.756</td>
<td>n-C₄</td>
<td>0.284</td>
</tr>
<tr>
<td>C₁</td>
<td>88.553</td>
<td>i-C₅</td>
<td>0.072</td>
</tr>
<tr>
<td>C₂</td>
<td>5.051</td>
<td>n-C₅ +</td>
<td>0.042</td>
</tr>
<tr>
<td>C₃</td>
<td>1.387</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The deionised water (dyed with methyl blue) with or without inhibitor was saturated
with natural gas at 104 bar in high-pressure cylinders to reduce the solubility effect
during injection. The cylinder content was shaken several times to promote gas
dissolution in the water and it was left overnight to equilibrate. 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 (104 bar – 109 bar). The system was filled with
natural gas at test pressure followed by reducing the system temperature to the
required temperature.
Flow test began by injecting pre-saturated solution and natural gas simultaneously at constant rate (0.1 cc/hr - 0.2 cc/hr) into the system through outlet (bottom) of micromodel using high-pressure quizix pump. The system temperature was reduced step by step if the hydrate had not been formed after more than 24 hours. Pressure inside the micromodel was maintained at 104 bar by backpressure regulator at the inlet (top) side. The formation of hydrate was visually observed and recorded accordingly. The measured and observed parameters are induction time and characteristic of hydrate build-up and deposits in the glass micromodel wall (e.g. no deposit, traces, thin hydrate layer, large deposits). In some cases, changes in differential pressure across micromodel due to hydrate blockage were measured. In this case, the blockage is defined as when the injection pressure has reached to the maximum set pressure limit (i.e. 156 bar). The induction time was measured from the time when the injection started at stabilised conditions of pressure and temperature.
Preliminary investigation on hydrate crystal particles size, distribution and plugging in the absence and presence of anti-agglomerant (labelled as HYTREAT04-106 and provided by Clariant Oil Services) with 3 mass% NaCl was studied using glass capillary tube. In this study, the micromodel system was modified to a single glass capillary tube (length of 112 mm and inside diameter of 0.5 mm), which connected to the 1-meter stainless steel tube inside the bath. In general, similar procedure was followed for preparing the system for injection as described above in the tests using multi-channels flow conduit. The changes in differential pressure, which indicate, hydrate formation and visual observation within the capillary tube was recorded for analysis. During the experiment, shut-in condition was also investigated by stopping the injection and closing all the valves. After 24 hours the injection was restarted until the maximum set point pressure limit was reached. Since the experiment is still on going at the time of report preparation, the results will be presented during Steering Committee Meeting.

2.3. RESULTS AND DISCUSSIONS

2.3.1. In the presence of PVCap base polymer
The experiments were conducted for the natural gas-water system with 1 mass% PVCap polymer (without solvent) at 109 bar under both flowing and static conditions. During the experiment, induction time was measured from the beginning of the injection at stabilised conditions, and the differential pressure across the micromodel was recorded. These data were used to indicate initial hydrate formation and duration for total blockage in the micromodel under flow conditions. 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 109 bar. Based on the differential pressure profile shown in Figure 2.2, it was observed that hydrate started to form after 0.7 hour of induction time at 13.7 °C (4.8 °C subcooling). The system pressure was continuously building-up due to gradual blockage of the flow tube as a result of hydrate deposition until the blockage occurred 85 hours after initial hydrate formation. The sequential still pictures are shown in Figure 2.3. As can be seen, hydrate formed both in gas and water phases.
Chapter 2 Micromodel Experiments

In some part of the glass conduit, the non-transparent hydrate turned into transparent hydrate crystals within 3 hours (Figure 2.3 (b)). Finally these crystals formed a continuous solid and non porous hydrate crystals which blocked the capillary tubes.

In the presence of 1 mass% PVCap, it appeared that the initial growth of hydrates occurred after approximately 20 hours of fluid injection at 13.7 °C as shown in Figure 2.4. Since there was no significant growth after 70 hours at that conditions, the system temperature was further reduced step by step at about 2 °C interval until catastrophic growth of hydrate was observed. The growth of hydrate occurred immediately after reaching 2 °C (16.5 °C subcooling). In this case, total blockage in the capillary tubes occurred after 40 hours of catastrophic growth of hydrate. 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 from images in Figure 2.5, hydrate began to form at the water-gas interface and grew inside the gas phase or bubbles with a non-transparent crystals (Figure 2.5(b)). After about 24 hours, these hydrate crystals turned into small transparent crystals within the gas profile (Figure 2.5(c)). Hydrate deposits appeared to be more porous with the formation of patches of hydrate crystals (Figure 2.5(d)). As time progressed, more hydrate formed which finally led to blockage within some part of capillary tubes. Similar test was repeated under static condition at 109 bar. The system temperature was reduced to 4.7 °C with no hydrate formation after leaving the system for 62 hours. Then the temperature was further reduced and hydrate formed at 3 °C (15.5 °C subcooling) in the presence of 1.0 mass% PVCap. Similar morphology (patches of hydrate crystals) as seen in the previous test was observed as indicated by images in Figure 2.6.

The natural gas hydrate crystals growth in the presence of 1 mass% PVCap with and without carrier fluid are compared in Figure 2.7. In the presence of PVCap with 1.5 mass% ethylene glycol as carrier fluid (Figure 2.7(a)), which was described in the earlier progress report, a continuous solid hydrate formed in the micromodel. On the other hand, without carrier fluid, thin patches of hydrate crystals was observed. The results of the observations in different systems are summarised in Table 2. The results suggest that the carrier fluid have some effect on the morphology of hydrate crystal at the tested condition.
## Table 2: Summary of Results: dried PVCap base polymer at 109 bar

<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>
<th>Comments (growth &amp; crystals morphology, etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>13.7</td>
<td>4.8</td>
<td>0.7</td>
<td>85</td>
<td>Continuous solid and non-porous hydrate crystals in both phases</td>
</tr>
<tr>
<td>Pure PVCap</td>
<td>13.7</td>
<td>4.8</td>
<td>20</td>
<td>-</td>
<td>Initial slow growth</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>16.5</td>
<td>0</td>
<td>40</td>
<td>Catastrophic growth in gas phase; patches of hydrate crystals in gas phase</td>
</tr>
<tr>
<td>Pure PVCap at static condition</td>
<td>3.0</td>
<td>15.5</td>
<td>-</td>
<td>-</td>
<td>Patches of hydrate crystals in gas phase</td>
</tr>
<tr>
<td>PVCap (in Luvicap + Ethylene glycol) at static condition</td>
<td>4.5</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>Continuous solid hydrate crystals in gas phase</td>
</tr>
</tbody>
</table>
Figure 2.2 Differential pressure profile for Natural Gas – Water system at 109 bar. Hydrate formed at 13.7°C (4.8°C subcooling).

(a) Before hydrate formation, $\Delta P = 0$ bar  
(b) 3 hrs after formation, $\Delta P = 30$ bar  
(c) 24 hrs after formation, $\Delta P = 190$ bar  
(d) 72 hrs after formation, $\Delta P = 730$ bar

Figure 2.3 Images of hydrate formation for Natural Gas-Water System at 109 bar, 13.7°C (4.8°C subcooling).
Figure 2.4. Differential pressure profile for Natural Gas – Water system in the presence of 1 mass% PVCap base polymer at 109 bar. Hydrate formed at 2.0°C (16.5°C subcooling).

(a) Before hydrate formation, $\Delta P = 0$ bar
(b) 3 hrs after formation, $\Delta P = 30$ bar
(c) 24 hrs after formation, $\Delta P = 240$ bar
(c) 72 hrs after formation, $\Delta P = 630$ bar

Figure 2.5 Images of hydrate formation for Natural Gas-Water System in the presence of 1 mass% PVCap polymer at 109 bar, 2.0°C (16.5°C subcooling) under flowing conditions.
Chapter 2 Micromodel Experiments

2.9

(a) Before hydrate formation                           (b) 3 hrs after formation

(c) 24 hrs after formation                                (c) 72 hrs after formation

Figure 2.6 Images of hydrate formation for Natural Gas-Water System in the presence of 1 mass% PVCap base polymer at 109 bar, 3.0°C (15.5°C subcooling) under static conditions.

Figure 2.7. Comparison of hydrate morphology for Natural Gas – Water system in the presence of 1 mass% PVCap (a) with carrier fluid (14 °C subcooling) (b) without carrier fluid (15.5 °C subcooling).
2.3.2. Effect of corrosion inhibitor

The objective of this work was to investigate the effect of corrosion inhibitor (CI) on the performance of kinetic hydrate inhibitor (KHI) using multichannel flow conduit under both static and flowing conditions. The experiment was performed using the mixture of 0.5 mass% PVCap (in 1.25 mass% LUVICAP®) and 500 ppm CI (Corrtreat 799). The results were compared with the earlier data reported for 0.5 mass% PVCap without corrosion inhibitor.

The differential pressure profile for Natural Gas – Water system in the presence of 0.5 mass% PVCap without corrosion inhibitor at 109 bar is presented in Figure 2.8. As shown in this figure, the initial growth of hydrate was observed at 8°C (11°C subcooling) after about 4 hours of fluid injection. However, there was no further growth of hydrate after leaving the system at this condition for 64 hours. Then, the system temperature was further reduced to 6°C (13°C subcooling) which induced catastrophic hydrate formation after 1.23 hours of induction time at this condition. Hydrate deposits initially appeared to be more porous (Figure 2.9(b)). As the time progressed, more hydrate formed which finally turned to a non-porous solid and led to blockage of capillary tubes (Figure 2.9(c)). In this case, total blockage in the capillary tubes occurred after 13.6 hours of catastrophic hydrate formation.

Similar procedure was repeated to investigate the effect of corrosion inhibitor. The differential pressure profile for Natural Gas – Water system in the presence of 0.5 mass% PVCap with corrosion inhibitor at 109 bar is presented in Figure 2.10. As shown in the figure, the catastrophic growth began after approximately 1.8 hours at 8°C (11°C subcooling). During the test, it was observed that many small gas bubbles were present in the glass conduit. It was also observed that from time to time there was a gas breakthrough in the system which redistributed hydrate particles or pushed it out of the conduit. This may explain the differential pressure fluctuations as observed in Figure 2.10. It should be noted that there was a sudden pressure drop at about 19 hours after injection. This was due to power failure which temporarily stopped the injection pump. The injection was continued and the pressure was built up which led to continuous hydrate formation within the conduit. After 26 hours, the system temperature was further reduced to 6°C (13°C subcooling). The increase in differential pressure suggested that more hydrate build-up formed in the conduit.
which continued until the temperature was further cooled down to 4 °C for several hours before terminating the test.

The above test was repeated by reducing system temperature directly to 6 °C (13 °C subcooling). The reason of repeating this test was to observe if the pressure fluctuation during previous flow test is typical characteristic in the presence of corrosion inhibitor and also to compare the time for blockage with result without corrosion inhibitor. As shown in Figure 2.11, the catastrophic growth of hydrate was observed after about 3 hours reaching the stabilised condition and similar fluctuation in pressure profile was observed. The induction time at this condition was slightly longer than that of test without corrosion inhibitor (1.23 hrs), which may be due to the direct cooling of the system to 6 °C. The time of blockage (47 hours) was also longer which may suggest slower rate of growth of hydrate. The sequential images of hydrate formation is presented in Figure 2.12. From these images, it was observed that hydrate formed both in water and gas phases. This suggest that PVCap failed to prevent hydrate formation in the water phase in the presence of the corrosion inhibitor.

Another test was carried out for this mixture of inhibitors under static conditions at 109 bar. Hydrate formed as soon as the temperature reached 4 °C (14.5 °C subcooling). Images of hydrate dissociation are shown in Figure 2.13. As shown in the Figure (Figure 2.13 (a)), the morphology of hydrate formation was a thin deposits of hydrate layer. It was observed that at this condition, hydrate formed from dissolved gas in the water phase.

The summary of the results is presented in Table 3. Based on these preliminary experiments, the results suggest that the presence of corrosion inhibitor affecting the performance of PVCap. This was observed from the fact that catastrophic hydrate formation began at 11 °C subcooling in the presence of corrosion inhibitor, while in the absence of CI, the catastrophic hydrate growth began at 13 °C subcooling. In addition, PVCap failed to prevent hydrate formation in the water phase in the presence of corrosion inhibitor.
Table 3: Summary of Results: Effect of corrosion inhibitor at 109 bar

<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>
<th>Comments (growth &amp; crystals morphology, etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUVICAP®</td>
<td>8</td>
<td>11</td>
<td>4 *</td>
<td>-</td>
<td>* Initial slow growth</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>13</td>
<td>1.23</td>
<td>13.6</td>
<td>Catastrophic growth of hydrate; non porous solid hydrate in gas phase</td>
</tr>
<tr>
<td>LUVICAP® + CI</td>
<td>8</td>
<td>11</td>
<td>1.8</td>
<td>-</td>
<td>Catastrophic growth of hydrate; small gas bubbles present; ΔP fluctuate</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>13</td>
<td>0</td>
<td>-</td>
<td>Catastrophic growth of hydrate; increase in ΔP due to hydrate build-up; terminate test at 4°C</td>
</tr>
<tr>
<td>LUVICAP® + CI at static condition</td>
<td>6</td>
<td>13</td>
<td>3</td>
<td>~ 47</td>
<td>Catastrophic growth of hydrate; hydrate formed in both phases</td>
</tr>
<tr>
<td>LUVICAP® + CI at static condition</td>
<td>4</td>
<td>14.5</td>
<td>0</td>
<td></td>
<td>Thin deposit of hydrate crystals in both phases</td>
</tr>
</tbody>
</table>

Figure 2.8. Differential pressure profile for Natural Gas – Water system in the presence of 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 2.9. Images of hydrate deposits for Natural Gas – Water system with 0.5 mass% PVCap at 109 bar, 6°C (13°C subcooling).

Figure 2.10. Differential pressure profile for Natural Gas – Water system in the presence of 0.5 mass% PVCap + 500 ppm Corrosion Inhibitor at 109 bar. Hydrate formed at 8°C (11°C subcooling). Differential pressure drop at 21 hours is due to power failure.
Figure 2.11. Differential pressure profile for Natural Gas – Water system in the presence of 0.5 mass% PVCap + 500 ppm Corrosion Inhibitor at 109 bar. Hydrate formed at 6°C (13°C subcooling).

Figure 2.12. Images of hydrate formation for Natural Gas-Water System in the presence of 0.5 mass% PVCap + 500 ppm Corrosion Inhibitor at 109 bar. Hydrate formed at 6°C (13°C subcooling) under flowing conditions.
Chapter 2 Micromodel Experiments

2.15

(a) $T = 4^\circ C$, $\Delta P = 5.5$ bar

(b) $T = 16^\circ C$, $\Delta P = 5$ bar

(c) $T = 19.4^\circ C$, $\Delta P = 1$ bar

(c) $T = 20^\circ C$, $\Delta P = 0.2$ bar

Figure 2.13. Images of hydrate dissociation for Natural Gas-Water System in the presence of 0.5 mass% PVCap + 500 ppm Corrosion Inhibitor at 109 bar. Hydrate formed at $4^\circ C$ (14.5$^\circ C$ subcooling) under static conditions.

2.4. SUMMARY OF RESULTS

A series of experimental studies were carried out to visually observe the hydrate growth patterns and plugging in the presence of PVCap base polymer. The experiments were conducted for natural gas-water system with 1 mass% PVCap base polymer at 109 bar under both flowing and static conditions. As expected, the presence of PVCap would slow down hydrate growth, delay blockage and also prevent hydrate formation in the water phase as compared to the blank test without inhibitor. Hydrate deposits appeared to be more porous with the formation of patches of hydrate crystals, both at flowing and static conditions.
The natural gas hydrate crystals growth in the presence of 1 mass% PVCap with and without carrier fluid were compared. While the results with carrier fluid shows that the hydrate crystals mainly exhibit continuous solid hydrate crystals, the test without carrier fluid exhibits thin patches of hydrate crystals. This suggests that the carrier fluid has some effect on the morphology of hydrate crystals at these test conditions.

The effect of the corrosion inhibitor (500 ppm CorrTreat 799) on the performance of the kinetic hydrate inhibitor (1.25 mass% LUVICAP®) under both static and flowing conditions was investigated. The results suggest that the presence of the corrosion inhibitor adversely affect the performance of PVCap, which confirms the results from the kinetic rig. This was observed from the fact that catastrophic hydrate formation began at 11°C subcooling in the presence of the corrosion inhibitor. On the other hand, in the test without the corrosion inhibitor hydrate formed at 13 °C subcooling. In addition, PVCap failed to prevent hydrate formation in the water phase in the presence of corrosion inhibitor.
CHAPTER 3
KINETICS RIG EXPERIMENTS

3.1. INTRODUCTION
In the previous period of the project, the performance of a new kinetic hydrate inhibitor (labelled as HYTREAT® 04-049 which is composed of the BASF advanced polymer, water and a solvent) was assessed in terms of induction time in natural gas-water system, by conducting experiments in a kinetic rig. Furthermore, the synergistic effects of different concentrations of a known synergist (Propylene Glycol Propyl Ether) and the impact of a commercial corrosion inhibitor on the performance of PVCap were studied.

In the last six months the synergistic effect of Propylene Glycol Propyl Ether on PVCap polymers with different lengths/molecular weights was studied. The inhibition effect of the combination of the BASF advanced polymer and PVCap in natural gas system at different degrees of subcooling was tested. Furthermore, the role of polymer carrier fluid in hydrate inhibition was studied by conducting experiments in a natural gas system in the presence of pure PVCap (dried LUVICAP®) and LUVICAP® (PVCap and ethylene glycol) at similar conditions. In another study, the performance of PVCap at subzero temperatures in the presence of 20 mass% ethylene glycol was tested. Finally the performance of a new anti-agglomerant in natural gas-water –condensate system was evaluated, using a novel helical tube mixer.

3.2. HYDRATE PHASE BOUNDARIES
The composition of the natural gas (LAB-NG) used in the experiments has been reported in Table 3.1. The hydrate phase boundaries for the natural gas –water system in the presence and absence of 20 mass% ethylene glycol were predicted by an in-house hydrate software (HWHYD) and are shown in Figure 3.1. Figure 3.1 was used for the calculation of degree of subcooling at the test conditions.
Table 3.1 The Composition of the natural gas used.

<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>88.553</td>
<td>5.051</td>
<td>1.387</td>
<td>0.182</td>
<td>0.284</td>
<td>0.072</td>
<td>0.042</td>
<td>2.673</td>
<td>1.756</td>
</tr>
</tbody>
</table>

Figure 3.1. Hydrate phase boundaries for natural gas-water system in the presence and absence of 20 mass% ethylene glycol.

### 3.3. SYNERGISM EFFECT OF PGPE ON DIFFERENT PVCAP POLYMERS

Very little work is published in regards to synergy and most information in regards to this area is taken from patents. A list of known and suspected synergistic chemicals taken from the patents is shown in Appendix C. As can be seen there is a great variety of chemicals that appear to have synergistic properties, including: corrosion inhibitors, quaternary onium salts, alcoholic and glycolic solvents. To the best of our knowledge, the only available published work in regards to the “synergy” phenomenon is attributed to Cohen et al (1997). This paper describes experimental work into the application of glycol ethers as synergists with vinylcaprolactam based polymers (PVCap, Gaffix VC-713®). The paper demonstrates that certain glycol ethers are effective synergists with these polymers, and concluded that the best chemical from this chemical family is 2-butoxyethanol (for Gaffix VC-713®). The paper also presents the idea of an optimum synergist concentration. The paper
concludes with the hypothesis that the hydrophobicity of the alkoxy group on the ether may associate/interact with the dissolved polymer and alter the polymer’s conformation in solution. This means that the glycol ether synergist keeps the polymer more open or unwound, and thus increases the surface area/active sites for inhibitor performance. This is the basis of this experimental work. To explore the above idea, it is required to be familiar with the nature of polymers in solution.

3.3.1. Polymers in Dilute Solution
The conformation of a polymer in a solution depends on a variety of factors, including interactions between solvent and polymer molecules, conformational effects arising from the polarity and steric bulk of the substituent groups, and restricted rotation caused by resonance, for example, of the type common to polyamides. Soluble polymeric molecules such as the common kinetic inhibitors in dilute solutions can be considered to be distinct, and do not interfere or entangle with each other, due to the spatial area involved. The molecules can also be considered as approximate spheres or balls due to the tendency of the polymers to self-associate. This self-association is reduced if the polymer is in a better solvent or if the temperature is raised. This has been illustrated in Figure 3.2.

It follows that if the self-association is increased, the specific surface area of the polymer exposed to the solution is lowered. The implication for this in regards to hydrate inhibition is that with better solvents/synergists, more polymer can be exposed to actively inhibit hydrate formation. This implies that careful selection of solvents is required to optimise the overall performance of polymeric kinetic hydrate inhibitors.

Figure 3.2. The effects of solvent power and temperature on a polymer molecule in solution. (Rosen, 1993)
It follows that as the polymer length increases, this self-association is increased, because the longer polymer is able to twist on itself to a greater extent. From this theory it is proposed that the longer the polymer, the larger the improvement in inhibition performance due to a presence of a specified synergist concentration. This is due to the fact that initially, the longer polymers will be self-associated to a greater extent than their shorter counterparts, and will be able to unwind to a larger extent in the presence of the synergist.

Based on the above hypothesis; a series of experiments were planned to examine the effect of a known synergist, on the kinetic inhibition performance of various lengths of a KHI.

3.3.2. Experimental Work
PVCap with Propylene Glycol Propyl Ether (PGPE) were selected for our inhibitor synergist mixture. This was based on experience of this system in previous studies, and primarily due to the availability of three different polymer lengths. The polymers used were supplied by BASF and are described below:

- LUVICAP® (2000-8000 Daltons, dry polymer)
- LUVISKOL® (~100,000 Daltons, 40% active polymer based in ethanol)
- LUBASIN® (~1,000,000 Daltons, 40% active polymer based in ethanol).

It was required to remove the commercial solvents from the above polymers to attain a dry polymer (LUVISKOL®, LUBASIN®). The polymers were separated via drying. This was achieved by heating the solution in an autoclave at 80°C for 2 days then the addition of water to further dilute the solvent. The polymer was heated at 90°C for 2 days, then at 100°C for 1 day. It was required to constantly break the surface of the polymer during drying. It is desirable to use flat large surface beakers for the drying. LUVICAP® was supplied dry, and thus there was no requirement for separation. A concentration of 1mass% active polymer with concentrations of 0%, 0.75% of Propylene Glycol Propyl Ether (PGPE), was made up with distilled water for the three polymers.

The tests were conducted in a 200ml, stirred, stainless steel, jacketed reactor (Kinetic Rig 4, detailed in Appendix A). The reactor was charged with 100ml of the specified solution and pressurised with natural gas. The vessel was then cooled, with the stirrer speed set to 600 rpm. To remove water history the temperature was raised to 32°C for 6 hours for LUVICAP®, and 26-28°C for 8 hours in regards to the heavier
Table 3.2. The results of the tests in kinetic rig 4 on natural gas-water system in the presence of different inhibitors /inhibitor and synergists. The pressure and temperature profiles of the tests are presented in Appendix B.

<table>
<thead>
<tr>
<th></th>
<th>Run</th>
<th>T (°C)</th>
<th>Pressure (bar)</th>
<th>Subcooling (°C)</th>
<th>Induction time (hrs)</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LUVICAP® 1%- no synergist</strong></td>
<td>1</td>
<td>7.3</td>
<td>105.352</td>
<td>11.1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.8</td>
<td>106.041</td>
<td>10.6</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8.1</td>
<td>106.179</td>
<td>10.3</td>
<td>0 (slow formation)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8.3</td>
<td>106.593</td>
<td>10.1</td>
<td>5.5</td>
<td>4</td>
</tr>
<tr>
<td><strong>LUVICAP® 1% with 0.75% PGPE</strong></td>
<td>1</td>
<td>7.6</td>
<td>100.870</td>
<td>10.5</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.6</td>
<td>100.112</td>
<td>11.5</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6.8</td>
<td>100.319</td>
<td>11.3</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.4</td>
<td>100.663</td>
<td>10.7</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td><strong>LUVICAP® 1% with 1.5% PGPE</strong></td>
<td>1</td>
<td>7.3</td>
<td>100.663</td>
<td>10.8</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.9</td>
<td>101.491</td>
<td>10.2</td>
<td>5.5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7.9</td>
<td>101.215</td>
<td>10.2</td>
<td>5.5</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8.4</td>
<td>101.767</td>
<td>9.8</td>
<td>No formation</td>
<td>12</td>
</tr>
<tr>
<td><strong>LUVISKOL® 1%- no synergist</strong></td>
<td>1</td>
<td>7.2</td>
<td>92.528</td>
<td>10.4</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.1</td>
<td>91.976</td>
<td>10.5</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7.3</td>
<td>92.289</td>
<td>10.3</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8.0</td>
<td>92.597</td>
<td>9.6</td>
<td>No Formation</td>
<td>16</td>
</tr>
<tr>
<td><strong>LUVISKOL® 1% with 0.75% PGPE</strong></td>
<td>1</td>
<td>5.5</td>
<td>89.218</td>
<td>11.9</td>
<td>0</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.7</td>
<td>89.080</td>
<td>11.7</td>
<td>1</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5.7</td>
<td>89.218</td>
<td>11.7</td>
<td>1.5</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.2</td>
<td>89.977</td>
<td>11.2</td>
<td>No Formation</td>
<td>20</td>
</tr>
<tr>
<td><strong>LUBASIN® 1%- no synergist</strong></td>
<td>1</td>
<td>9.0</td>
<td>92.321</td>
<td>8.6</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.9</td>
<td>92.252</td>
<td>8.7</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9.3</td>
<td>92.941</td>
<td>8.3</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>9.3</td>
<td>92.941</td>
<td>8.2</td>
<td>No formation</td>
<td>24</td>
</tr>
<tr>
<td><strong>LUBASIN® 1% with 0.75% PGPE</strong></td>
<td>1</td>
<td>8.3</td>
<td>99.216</td>
<td>9.8</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9.2</td>
<td>99.836</td>
<td>9.9</td>
<td>No formation</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8.8</td>
<td>99.629</td>
<td>9.3</td>
<td>0</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>9.3</td>
<td>99.836</td>
<td>8.8</td>
<td>No formation</td>
<td>28</td>
</tr>
</tbody>
</table>
LUVISKOL® and LUBASIN®. This heating temperature was reduced to minimise the risk of polymer deposition onto the metallic surfaces of the rig which was witnessed in previous experiments (with LUVISKOL®). Tests were conducted to determine the maximum subcooling that the specified inhibitor solutions could delay the onset of hydrate growth and nucleation. Table 3.2 shows the results of the experimental work carried out in kinetic rig 4 for the various inhibitors, and inhibitor plus synergist solutions. The pressure and temperature profiles for these tests are available in Appendix B, under the figure numbers outlined in the Table 3.2. Further tests are planned for both LUVISKOL® and LUBASIN® with 1.5% PGPE. They will be presented at the upcoming JIP steering meeting.

In Table 3.3 the summary of the results is shown, with the emphasis based on the temperature at which the induction time almost disappears i.e. less than 120 minutes. This value of subcooling taken is the arithmetic average between a point of “no induction” (t<2 hours), and a point where there is a significant induction time (t>2 hours).

Table 3.3. Synergism effect of different concentrations of PGPE on different PVCap polymer lengths.

<table>
<thead>
<tr>
<th></th>
<th>0% PGPE</th>
<th>0.75% PGPE</th>
<th>1.5% PGPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUVICAP®</td>
<td>10.5°C</td>
<td>10.9°C</td>
<td>10.5°C</td>
</tr>
<tr>
<td>LUVISKOL®</td>
<td>10.4°C</td>
<td>11.5°C</td>
<td>10.6%</td>
</tr>
<tr>
<td>LUBASIN®</td>
<td>8.3°C</td>
<td>9.0°C</td>
<td>8.4%</td>
</tr>
</tbody>
</table>

The results show that there is a marked improvement in inhibitor performance in the presence of 0.75% PGPE in both of the longer polymers, at 10.6% and 8.4% for LUVISKOL® and LUBASIN® respectively. There was a negligible improvement of 3.8% for the shorter LUVICAP® polymer in the presence of 0.75% PGPE. This follows the theory that the synergists enable the larger polymers to unwind to a larger extent.

In the presence of 1.5% PGPE the performance of LUVICAP® was reduced by 3.7%. This follows the notion of an optimum inhibitor concentration; which may have already been passed (Cohen et al., 1998). This data suggests that too much of a solvent or synergist may become an antagonist to the inhibitors- this is seen for methanol; which becomes antagonistic at high concentrations (Sloan et al, 1998).
From previous study as part of this joint industry project it was concluded that shorter length polymers were more effective at inhibition than their longer counterparts. This is primarily due to the fact that the shorter the polymer has a larger surface area exposed to the solution, for the same mass of polymer i.e. compare LUBASIN® (1,000,000 Daltons) and LUVISKOL® (100,000 Daltons) there are 1:10 polymer units for the same mass %. This was witnessed again for the synergy free polymer solutions.

It is clear that the synergists affect polymers of different lengths in different ways, and the fact that the data shows that the longer polymers attained a substantial increase in performance as opposed to their shorter counterpart, may suggest that there is some validity to the proposed theory. Further work is needed to investigate the effect of different synergistic chemicals on different lengths of polymers, to verify these results.

It is proposed that the reason why the glycol ethers are good synergists may be due to their chemical structure; they have both an ether group and an alcohol group. It is envisaged that chemicals such as methanol (one polar group) may associate with the lactam group and get in the way of the polymer from self-associating, and thus increase the volume of the polymer. It is proposed that with the two polar groups the glycol ethers may be able to associate to two lactam rings and “wedge” the polymer strands apart, and thus increase the volume of the polymer to a much greater extent.

3.4 TESTING THE INHIBITION EFFECT OF THE COMBINATION OF BASF ADVANCED POLYMER AND PVCAP

In the last steering committee meeting it was decided to test the inhibition effect of the combination of the two inhibitors; BASF advanced polymer and PVCap in bulk conditions. A series of tests were conducted in kinetic rig 2 (detailed in Appendix A) on a natural gas-water system in the presence of 1.25 mass% LUVICAP® (containing 0.5 mass% PVCap) and a mixture of 2.5 volume% of HYTREAT® 04-049 (composed of the BASF advanced polymer, water and a solvent). The experiments were carried out in the pressure range of 100-102 bar and a subcooling range of 13.2-14.1 °C, with a mixing rate of 600 rpm. The results of the experiments have been summarised in Table 3.4 and the pressure and temperature profiles of the tests have been presented in Appendix B (Figures 29-34). As seen in Table 3.4, in the presence of 0.5 mass% PVCap and at 13.2 °C subcooling the induction time is about 3-5 hours (Tests No.1-
2). Addition of 2.5 volume percent of HYTREAT® 04-049 to the system at similar conditions (13.3 °C subcooling) extended the induction time to 13-14 hours (Tests No.3-4) and at higher degrees of subcooling (13.7 °C) 9-11 hours induction time was achieved by the combination of the inhibitors (Tests No.5-6). In the last progress report the performance of 5 volume percent of HYTREAT® 04-049 in natural gas-water system at 100 bar and different degrees of subcooling was presented. It appeared that in the presence of 5 volume percent of HYTREAT® 04-049 at 13.2-13.6 °C subcooling the induction time was less than 7 hours. Comparing the test results (Table 3.4, Tests No.3-6), it seems that for the mentioned test conditions, the hydrate inhibition effect of a mixture of 0.5 mass% PVCap and 2.5 volume% of HYTREAT® 04-049 is better than that of 5 volume% of HYTREAT® 04-049.

Table 3.4. Experimental results obtained from the kinetic rig 2 for PVCap and the mixture of PVCap and (HYTREAT04-049) solution in the presence of natural gas at 600 rpm mixing rate.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>PVCap mass%</th>
<th>HYTREAT® (04-049) vol%</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>0.5</td>
<td>0</td>
<td>5.5 / 102</td>
<td>13.2</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0</td>
<td>5.5 / 102</td>
<td>13.2</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>2.5</td>
<td>5.3 / 101</td>
<td>13.3</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>2.5</td>
<td>5.3 / 101</td>
<td>13.3</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>2.5</td>
<td>4.8 / 100</td>
<td>13.7</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>2.5</td>
<td>4.8 / 100</td>
<td>13.7</td>
<td>9</td>
</tr>
</tbody>
</table>

3.5. THE ROLE OF POLYMER CARRIER FLUID

It is believed that the carrier fluid may mask the basic properties of the polymer. In the last steering committee meeting it was suggested to investigate the effect of carrier fluid on hydrate inhibition. In this study the inhibition effect of dried LUVICAP® (2000-8000 Dalton, PVCap) in natural gas-water system was tested and compared with LUVICAP® (containing 60 mass% ethylene glycol and 40 mass% PVCap). The results of the tests carried out in kinetic rig 5 (detailed in Appendix A) have been summarised in Table 3.5 and the pressure and temperature profile of the experiments are presented in Appendix B (Figures 35-39). As seen in Table 3.5, the experiments were carried out at 100 bar and a subcooling range of 12.9-13.3 °C, and the induction times are very close for both cases (with and without ethylene glycol). For comparison the pressure profiles of the tests have been shown together in Figure 3.3. As can be seen in the figure, after 20 hours, the rate of growth in the presence of 1.5
mass% ethylene glycol is higher compared to the tests with pure PVCap. It seems that in the conditions that the experiments were carried out, ethylene glycol slightly decreases the inhibition effect of PVCap.

Table 3.5. Experimental results obtained from the kinetic rig 5 for 1 mass% pure PVCap in water in the presence and absence of carrier fluid (ethylene glycol) at similar conditions in natural gas system at 600 rpm mixing rate.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Ethylene Glycol%</th>
<th>Testing T/P</th>
<th>Subcooling / °C</th>
<th>Induction Time / hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>5.0 / 101</td>
<td>13.1</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>4.8 / 100</td>
<td>13.3</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>5.0 / 100</td>
<td>13.1</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>5.2 / 100</td>
<td>12.9</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>4.9 / 100</td>
<td>13.2</td>
<td>27</td>
</tr>
</tbody>
</table>

Figure 3.3. Pressure profiles of the experiments summarised in Table 3.5.

3.6. THE PERFORMANCE OF KHI IN SUBZERO CONDITIONS
Onshore pipelines could be subjected to subzero conditions; hence thermodynamic and/or kinetic hydrate inhibitors are needed to prevent hydrate and ice formation. In
this study the inhibition effect of PVCap in natural gas-water system below the ice point was tested. In order to prevent ice formation, and providing similar degrees of subcooling at the same pressure range but different temperatures, ethylene glycol (20 mass%) was added to water. It should be mentioned that methanol was not used for this purpose as it has been reported to have adverse effect on the performance of PVCap (Sloan et al, 1998).

The presence of ethylene glycol was taken into account in calculation of degrees of subcooling (Figure 3.1) in the experiments. A total of six tests were conducted in kinetic rig 1 (detailed in Appendix A) charged with natural gas and a solution of 20 mass% ethylene glycol and 1 mass% PVCap in water. The tests carried out in a pressure range of 90-94 (bar) at different degrees of subcooling. The results of the tests have been summarised in Table 3.6 and the pressure and temperature profile of the experiments are presented in Appendix B (Figures 40-45). As seen in Table 3.6, the experiments were started with test at –1.3 °C and 90 bar (13.2 °C subcooling) where induction time longer than 30 hours was observed (Test No.1). In the subsequent tests the degree of subcooling was increased step by step to 15.5 °C, where no induction time was observed. It seems that for a natural gas-water system, 1 mass% PVCap in the presence of 20 mass% ethylene glycol can inhibit hydrate formation at temperatures below ice point. For comparison two tests were conducted in a natural gas-water system in the presence of 2.5 mass% LUVICAP® (1 mass% PVCap and 1.5 mass% EG) at similar pressure and degrees of subcooling (13.3 °C). The pressure and temperature profiles of the tests are presented in Appendix B (Figures 46-47). Figure 3.4 shows the comparison of the pressure profiles of the tests in the presence of 1 mass% PVCap with 20 and 1.5 mass% ethylene glycol. As shown in Figure 3.4, at similar degrees of subcooling (13.3-13.4 °C), in the presence of 20 mass% EG, longer induction time and lower rate of growth compared to 1.5 mass% EG are observed. Similar pressure profiles were observed by increasing the subcooling to 15 °C. While further tests are needed, the preliminary results show that 20 mass% ethylene glycol has a positive effect on the performance of PVCap.
Table 3.6. Experimental results obtained from the kinetic rig 1 for 1 mass% PVCap in water in the presence of 20 mass% ethylene glycol at subzero temperatures in natural gas system at 600 rpm mixing rate.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Ethylene Glycol%</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>20</td>
<td>-1.3 / 90</td>
<td>13.2</td>
<td>&gt;30</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>-1.3 / 95</td>
<td>13.5</td>
<td>&gt;30</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>-3.0 / 92</td>
<td>15</td>
<td>&gt;30</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>-3.2 / 90</td>
<td>15.1</td>
<td>&gt;20</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>-3.3 / 96</td>
<td>15.5</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>-3.4 / 94</td>
<td>15.6</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 3.4. Pressure profiles of the experiments in natural gas-1 mass% PVCap in water system at temperatures above and below zero °C.

3.7. EVALUATION OF A NEW ANTI-AGGLOMERANT BY APPLICATION OF A HELICAL TUBE MIXER IN THE KINETIC RIG

The application of the helical tube mixer in a kinetic rig for evaluation of anti-agglomerants in condensate-water-natural gas systems has already been presented. In previous experiments carried out in natural gas-water systems various rates of mixing were used; to standardise the data it was decided to adopt the rate of 400 rpm for all further tests. This value was selected for condensate systems because of better mixing efficiency, and a more stable torque response to the rheological changes of the
In this study the performance of a new anti-agglomerant (labelled as HT04-106 and provided by Clariant Oil Services) in a natural gas-water-condensate system is evaluated. The helical tube mixer installed in kinetic rig 5 (detailed in Appendix A) was used for the experiments. A North Sea Field condensate was used in the tests. A total of four experiments were conducted in kinetic rig 5 with a mixing rate of 400 rpm. A solution of 33 volume % water in natural gas condensate was used in the tests in the presence and absence of an anti-agglomerant (HT04-106). The first two tests were carried out in the absence of AA. The profiles of the first test are shown in Figure 3.5. As shown in the figure, the test started at 120 bar and 34.6 °C, where torque was about 36 (arbitrary unit). The system was then cooled down and when hydrate formed at about 13 °C and 100 bar (5.2 °C subcooling with respect to natural gas-water hydrate phase boundary), torque was then increased to 111 and after one hour it was stabilised at 106. By increasing the temperature to 34°C, torque was reduced to its initial value 36. By repeating the above test, good repeatability of data was observed. The results of the repeat test are presented in the Appendix B (Figure 48).

![Figure 3.5. Pressure, temperature and torque profiles for Condensate-NG-water system, rig 5, helical mixer, rpm=400.](image-url)
The above tests were repeated in the presence of 0.5 mass % of the anti-agglomerant (HT04-106). The results of the first test are shown in Figure 3.6 and the results of the repeat test are presented in the Appendix B (Figure 49). As shown in Figure 3.6, after hydrate formation (at 10°C and 102 bar equivalent to 8.2°C subcooling with respect to natural gas-water hydrate phase boundary) torque increased to 112. After two hours between 105-112, it later dropped to 30 and within 5 hours it was stabilised at 41. In comparison to the test without AA (Figure 3.5), after hydrate formation the same maximum torque was observed, however it was reduced to 41 after 2 hours. The stabilised torque after hydrate formation in the presence of anti agglomerant (41) is much less than that of blank test (106) denoting the transportability of the hydrate slurry.

![Graph showing pressure, temperature, and torque profiles](image)

Figure 3.6. Pressure, temperature and torque profiles for NG-Condensate-Water system in the presence of 0.5 mass% AA (HT04-106) in water phase. W/C=0.33, kinetic rig 5, helical tube mixer, rpm=400.

### SUMMARY

Tests were carried out to investigate the effect of the synergist Propylene Glycol Propyl Ether on the hydrate inhibition performance of different lengths of PVCap. The results demonstrate that the change in kinetic hydrate inhibition of the longer polymers is much better in comparison to the shorter polymers. The performance of
the larger polymers were of the same magnitude, possibly implying that after a certain length of polymer is reached the effect of the synergistic chemicals will be the same. The inhibition effect of the combination of two kinetic hydrate inhibitors; BASF advanced polymer and PVCap in natural gas–water system in bulk conditions was tested. The test results showed that the hydrate inhibition effect of a mixture of 0.5 mass% PVCap and 2.5 volume% of HYTREAT® 04-049 (containing BASF advanced polymer) is better than that of 5 volume% of HYTREAT® 04-049.

The role of polymer carrier fluid in hydrate inhibition was studied by conducting experiments in a natural gas system in the presence of pure PVCap (dried LUVICAP®) and LUVICAP® (PVCap and ethylene glycol) at similar conditions. The results showed that, at the experimental conditions 1.5 mass% ethylene glycol slightly decreases the inhibition effect of PVCap.

The inhibition effect of PVCap in natural gas-water system below at subzero conditions was tested. In order to prevent ice formation, ethylene glycol (20 mass%) was added to water. The tests results showed that for natural gas-water system, 1 mass% PVCap in the presence of 20 mass% ethylene glycol could inhibit hydrate formation at subzero temperatures. While further tests are needed, the preliminary results showed that 20 mass% ethylene glycol has a positive effect on the performance of PVCap.

The performance of a new anti-agglomerant (HT04-106) in a natural gas-water-condensate system was evaluated with torque measurements in a kinetic rig equipped with a helical tube mixer. Two series of tests in the presence and absence of AA were conducted. Similar maximum torques were observed for both cases, however the stabilised torque after hydrate formation in the presence of anti-agglomerant was much lower than that of the blank test, denoting the transportability of the hydrate slurry.

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 justification for this is to complement 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.

Within the last six months tests have been conducted to find the effect of PVCap polymer on the growth pattern of hydrates formed from natural gas in a high pressure visual cell under static conditions. This work was done in order to support work on other rigs and to complete the picture regarding observations made in previous work on the effect of LUVICAP® on the growth pattern of natural gas hydrates. In previous work tests had shown that the pattern of natural gas hydrate growth was significantly different between tests with distilled water and with LUVICAP®. LUVICAP® is composed of a polymer (PVCap) and ethylene glycol and hence it was decided to find the effect of ethylene glycol on its own and the polymer on its own. In the previous project progress report the effect of ethylene glycol on the growth pattern of natural gas hydrates was reported and to complete the data set the effect of the polymer alone was studied and the results are presented in this report.

The high pressure visual rig can also be used to measure interfacial tension (IFT) using the pendant drop technique. Measurements have been made of the IFT between aqueous and vapour phases in the systems methane with an aqueous solution of a kinetic hydrate inhibitor, HYTREAT®04-049 (composed of the BASF new advanced polymer, water and a solvent), and methane with an aqueous solution of another kinetic hydrate inhibitor, HYTREAT®03-187, which includes PVCap, a synergist chemical, water and ethylene glycol. The results of this work are presented in this
report. Measurements are in progress to investigate the effect of the PVCap polymer alone on IFT in a methane-water system. In addition it is planned to measure the effect of the new Anti-Agglomerant on the IFT between gas and water and liquid hydrocarbon and water in a liquid water-liquid hydrocarbon gas system. It is planned to present the results of these studies at the project steering committee meeting in June.

### 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 517bar 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.

**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 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>2.67</td>
</tr>
<tr>
<td>C₁</td>
<td>88.55</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.76</td>
</tr>
<tr>
<td>C₂</td>
<td>5.05</td>
</tr>
<tr>
<td>C₃</td>
<td>1.39</td>
</tr>
<tr>
<td>iC₄</td>
<td>0.18</td>
</tr>
<tr>
<td>nC₄</td>
<td>0.28</td>
</tr>
<tr>
<td>iC₅</td>
<td>0.07</td>
</tr>
<tr>
<td>nC₅⁺</td>
<td>0.04</td>
</tr>
</tbody>
</table>

4.3 EXPERIMENTAL RESULTS AND OBSERVATIONS OF THE GROWTH PATTERN OF NATURAL GAS HYDRATES WITH PVCAP POLYMER AND NATURAL GAS

The cell was loaded with an aqueous solution composed of 1 mass% PVCap polymer and natural gas. The cell was cooled from 35°C to 4°C over 18 hours. At 4°C and the cell pressure of 106 bar the system was around 14.5°C inside the hydrate stability zone (i.e., degree of subcooling=14.5°C). 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 previous data recorded for tests with 2.5 mass% LUVICAP® and 1.5 mass% ethylene glycol. As can be seen from Figure 4.2 there are differences between the patterns of the pressure time data between the three tests. The first thing to note is that the temperature in the test with 1 mass% PVCap polymer was reduced from 35°C to 4°C over 18 hours whereas in the other two tests this temperature reduction was over 12 hours. In the tests with 1 mass% PVCap polymer and 1.5 mass% ethylene glycol there was some induction time prior to hydrate formation. This was not the case in the test with 2.5 mass% LUVICAP®, hydrate formation starting close to when the cell temperature reached 4°C. Once
hydrate formation had started the test with 1.5 mass% ethylene glycol showed the most rapid rate of pressure decline with time. The initial fast rate slowed after the pressure had reduced to around 80 bar. The rate of pressure reduction on initial formation was similar for the tests with 2.5 mass% LUVICAP® and 1 mass% PVCap polymer. In the test with 2.5 mass% LUVICAP® there was an increase in the rate of pressure reduction with time after around 30 hours from the start of the test.

![Figure 4.2](image)

Figure 4.2 Pressure and time data for tests with natural gas in the presence of 1 mass% PVCap polymer, natural gas in the presence of 1.5 mass% ethylene glycol, and natural gas in the presence of 2.5 mass% LUVICAP®.

From a visual point of view the overall pattern of hydrate formation was similar in all cases. Hydrate formation started at the gas/water interface and on the cell walls in the upper part of the cell. Water appeared to be drawn from the lower part of the cell to the upper part of the cell leading to the bulk of hydrate formation occurring in the upper part of the cell. In the test with 1.5 mass% ethylene glycol the hydrates formed rapidly at the gas/water interface and gas bubbles appeared below the interface, hydrate formation continuing rapidly at all of the gas/water interfaces. In both of the test with the polymer the formation of hydrates at the gas water interface was not as rapid and gas bubbles did not appear below the interface.
In both tests with the polymer the growth pattern was similar, however in the test with the polymer alone the hydrates appeared to have a more grainy appearance as if many smaller crystals had formed. As hydrate formation occurred in the upper part of the cell and water was drawn up the cell the layer of hydrates formed at the original gas/water interface appeared to break up leaving pieces of hydrate that appeared to be conical in shape. Figures 4.3 and 4.4 show pictures of the start of hydrate formation. Figure 4.5 shows the grainy appearance of the hydrates and Figures 4.6 and 4.7 show the hydrate pieces left after the break up of the original hydrate layer.

Figure 4.3  Picture showing the start of natural gas hydrate formation at the gas/water interface in the test with natural gas and an aqueous solution comprised of 1 mass% PVCap polymer.
Figure 4.4 Picture showing the start of natural gas hydrate formation at the gas/water interface in the test with natural gas and an aqueous solution comprised of 1 mass% PVCap polymer. The hydrates can be seen forming across the whole gas/water interface.

Figure 4.5 Picture showing the grainy appearance of the natural gas hydrates formed in the test with natural gas and an aqueous solution comprised of 1 mass% PVCap polymer.
Chapter 4  High Pressure Visual Rig Experiments

Figure 4.6  Picture showing the pieces of hydrate left after the break up of the solid layer originally formed at the gas/water interface in the test with natural gas and an aqueous solution comprised of 1 mass% PVCap polymer.

Figure 4.7  Picture showing a piece of hydrate left after the break up of the solid layer originally formed at the gas/water interface in the test with natural gas and an aqueous solution comprised of 1 mass% PVCap polymer.
4.4 EXPERIMENTAL EQUIPMENT AND METHODS-INTERFACIAL TENSION MEASUREMENTS

The same visual rig as described above and shown in Figure-4.1 was modified to make IFT measurements. A hypodermic needle was welded into a high-pressure fitting and inserted into one of the four available ports. A valve was fitted to the outlet from the port and the valve outlet blanked off. Opening the valve allows a small amount of liquid to be drawn into the hypodermic needle and conversely closing the valve ejects the liquid from through the needle. The cell was positioned on the pivot in such a way that the phase of interest, water or liquid hydrocarbon, surrounded the point of the needle and a sample was then taken into the valve-needle set-up. The cell was then oriented to allow a drop to be formed in the second phase of interest whether water in oil or water in gas. A magnifying camera was set up to take video of the drops. A video capture card was then used to capture still images of the pendant drops. An example of a pendant drop is shown in Figure-4.8.

The IFT is calculated from the dimensions of the pendant drop as described by Andreas et al (1938). The required measurements are shown in Figure-4.9 and Equation-4.1 is used to calculate the IFT.

Figure 4.8 Example of pendant drop of water in methane.
Equation-4.1

\[ \text{IFT} = \Delta \rho \cdot g \cdot \frac{d e^2}{H} \]

\[ \Delta \rho \text{ difference in density between phases} \]
\[ g \text{ gravity constant} \]
\[ H \text{ shape factor obtained from look-up tables based upon ratio of ds/de} \]

4.5 RESULTS OF IFT MEASUREMENTS

Two sets of IFT measurements were made between the aqueous and vapour phases. In both cases the gas was methane. In one set an aqueous solution comprised of 5 mass% HYTREAT®04-049 (BASF advanced polymer based KHI) and in the other an aqueous solution of 5 mass% HYTREAT®03-187 (PVCap based KHI) was used. In both cases measurements were made at different pressures at a temperature of 10°C. The experimental measurements for the system with 5 mass% HYTREAT®04-049 are shown in Table 4.2 and for the system with 5 mass% HYTREAT®03-187 are shown in Table 4.3. Figure 4.10 is a plot of the experimental data from this current work and previous data for methane with distilled water and methane with 2.5 mass% LUVICAP® for comparison purposes.
Table 4.2  IFT values for water/methane in the aqueous solution comprised of 5 mass\% HYTREAT®04-049.

<table>
<thead>
<tr>
<th>Pressure bar ±0.5</th>
<th>IFT mN.m⁻¹ ±1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>32</td>
</tr>
<tr>
<td>5.3</td>
<td>28</td>
</tr>
<tr>
<td>10.1</td>
<td>29</td>
</tr>
<tr>
<td>17.4</td>
<td>28</td>
</tr>
<tr>
<td>35.8</td>
<td>26</td>
</tr>
<tr>
<td>45.6</td>
<td>21</td>
</tr>
<tr>
<td>74.9</td>
<td>21</td>
</tr>
<tr>
<td>101.7</td>
<td>17</td>
</tr>
<tr>
<td>120.1</td>
<td>17</td>
</tr>
</tbody>
</table>

Table 4.3  IFT values for water/methane in the aqueous solution comprised of 5 mass\% HYTREAT®03-187.

<table>
<thead>
<tr>
<th>Pressure bar ±0.5</th>
<th>IFT mN.m⁻¹ ±1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>33</td>
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<tr>
<td>5.9</td>
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</tr>
<tr>
<td>10.7</td>
<td>36</td>
</tr>
<tr>
<td>18.4</td>
<td>34</td>
</tr>
<tr>
<td>36.3</td>
<td>35</td>
</tr>
<tr>
<td>63.2</td>
<td>28</td>
</tr>
<tr>
<td>86.1</td>
<td>29</td>
</tr>
<tr>
<td>97.9</td>
<td>29</td>
</tr>
<tr>
<td>119.8</td>
<td>27</td>
</tr>
</tbody>
</table>
4.11

Figure 4.10  Summary of experimental IFT data between methane and distilled water and methane and different aqueous solutions of hydrate inhibitors.

4.6 REFERENCES

Andreas, J.M., Hauser, E.A. and Tucker, W.B., Boundary Tension by Pendant Drops, Presented at the Fiftieth Colloid Symposium held at Cambridge, Massachusetts, June 1938.
CHAPTER 5

HYDRATE NUCLEATION TESTS USING ULTRASONIC WAVES

5.1. INTRODUCTION

In our previous study it has been found that certain carrier fluids of kinetic hydrate inhibitors, for example, ethylene glycol, may play an important role in the performance of kinetic hydrate inhibitors. The visual observations in the visual kinetic rig showed that ethylene glycol prevents the formation of a solid hydrate layer that is capable of halting the flow of water to hydrates growing in the upper part of the cell. The results of the nucleation tests using the ultrasonic rig showed the different inhibition characteristics of PVCap (LUVICAP®) and the BASF Advanced Polymer (HYDREAT 04-049). The advanced polymer seems to strongly hinder hydrate nucleation, while PVCap is more effective at inhibiting hydrate formation and delaying catastrophic growth. The nucleation tests also demonstrated that the synergistic chemical, Propylene Glycol Propyl Ether (PGPE), significantly improves the performance of both PVCap and BASF Advanced Polymer.

In regards to the above work, further nucleation tests in the ultrasonic rig have been carried out. Firstly, one test was conducted with dried LUVICAP® to examine the effect of ethylene glycol as a carrier fluid on hydrate inhibition. Next, the performance of the combination of PVCap with BASF Advanced Polymer was investigated. Finally, two synergists with identical molecular formula and different structures, Ethylene Glycol Monobutyl Ether (EGME) and Ethylene Glycol Diethyl Ether (EGDE), were tested to study the effect of molecular structure of synergistic chemicals on the performance of PVCap. In all these tests, a natural gas with typical composition was used as a hydrate former.

5.2. 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
LUVICAP® (Dried Version) supplied by BASF Company
BASF Advanced Polymer (HYTREAT 04-049) supplied by Clariant Oil Services
Ethylene Glycol Monobutyl Ether (98%) and Ethylene Glycol Diethyl Ether (99+) supplied by Aldrich Chemical Company, Inc.

Distilled water

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol%</th>
<th>Component</th>
<th>Mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>88.553</td>
<td>i-C5</td>
<td>0.072</td>
</tr>
<tr>
<td>C2</td>
<td>5.051</td>
<td>n-C5+</td>
<td>0.042</td>
</tr>
<tr>
<td>C3</td>
<td>1.387</td>
<td>CO2</td>
<td>1.756</td>
</tr>
<tr>
<td>i-C4</td>
<td>0.182</td>
<td>N2</td>
<td>2.673</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.284</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.3. METHOD AND PROCEDURE

After applying vacuum to the rig, a certain amount of the test solution was sucked into the test cell, then the natural gas was injected into the cell through a piston vessel until the desired pressure of about 125 bar was reached at room temperature. The system was kept at 21 °C for more than 12 hours to gain thermodynamic equilibrium. In the tests the system was directly cooled down to the target temperature: 4 °C in the cooling bath. The system temperature and pressure were logged on a PC through RS-232 interface, and the ultrasonic waveforms were displayed and recorded by the same PC through a digital storage oscilloscope.

As described in the previous reports, all tests were performed at a constant volume of gas to liquid ratio in the cell: about 71 vol% of liquid phase and 29 vol% of gas phase. This is to allow most of acoustic energy to propagate through the liquid phase, and ensure an identical contact area of the hydrate former with the water for all of the tests. To exclude the undesirable effect of different initial thermodynamic conditions on gas hydrate nucleation and growth, all tests were started at the same thermodynamic conditions. Figure 5.1 shows the hydrate phase boundary of the natural gas-water system and the initial conditions. All the tests were conducted in bulk and static conditions.
5.4. RESULTS AND DISCUSSIONS

5.4.1 Comparison of PVCap With and Without Ethylene Glycol As a Carrier

The dried version of LUVICAP® was tested at about 115 bar and 4 °C corresponding to a subcooling of 15 °C for the natural gas-water system. Figure 5.2 shows the result of the test with 0.5 mass% of the dried LUVICAP®. Figure 5.2a shows the profile of the system pressure; as can be seen the system pressure smoothly decreased as the system was cooled down, and there was no meaningful pressure drop to indicate hydrate formation at 4 °C. However, Figure 5.2b shows the response of the pressure and ultrasonic signals in detail. Continuous drop of the FFT and the amplitude indicated that hydrate nucleation started at 1.2 hours (11.0 °C and 117.1 bar). It is most likely that after the nucleation, natural gas quickly formed a thin hydrate layer at the interface between the gas and the liquid phase, which prevented hydrates from growing into the bulk of the liquid phase. After the temperature reached 4 °C the continuity of the FFT and the amplitude decline suggests hydrate formation.

In comparison to the previously reported results in the test with LUVICAP® (40 mass% PVCap and 60 mass% ethylene glycol), it can be seen in Figure 5.3 that hydrate nucleation started at around 1.8 hours (7 °C and 114 bar), slow formation started at 2.6 hour (4 °C and 111 bar), and catastrophic growth started at 7 hours (4 °C and 105 bar), i.e., about 1 hour of nucleation time and nearly 5 hours of catastrophic growth delay. Additionally, quite a lot of hydrates grew into the bulk of the liquid.
phase, which resulted in significant attenuation of the ultrasonic signal. It seems clear that at static conditions the presence of ethylene glycol as a carrier altered the performance of PVCap and caused more hydrates to be formed in the liquid phase, but it had little influence on the nucleation.

Figure 5.2  Hydrate nucleation and growth in the presence of 0.5 mass% of PVCap (dried version of LUVICAP®) (Legend: P=Pressure, T=Temperature, A=Amplitude).
5.4.2 Combination of PVCap and BASF Advanced Polymer

It may be possible to improve the capability of PVCap to prolong its nucleation time by combination of PVCap and BASF Advanced Polymer, as the previous nucleation tests suggested that the advanced polymer was likely to strongly hinder hydrate nucleation, while PVCap was more effective at inhibiting hydrate formation and delaying catastrophic growth. To examine this, two tests were conducted with 0.5 mass% of PVCap (1.25 mass% of LUVICAP®) plus 1 vol% and plus 2.5 vol% of BASF Advanced Polymer (HYDREAT 04-049, density 1.07 g/cm³), respectively.

Figure 5.4 shows the results of the test with 0.5 mass% of PVCap (1.25 mass% of LUVICAP®) plus 1 vol% of BASF Advanced Polymer. In Figure 5.4b the FFT drop indicates hydrate nucleation started at 0.6 hours (15.6 °C and 121 bar). The pressure started declining at 3.2 hours (33.8 °C and 110 bar) due to hydrate formation, and the catastrophic growth started at 9.6 hours (3.8 °C and 95.3 bar). The nucleation time is about 2.6 hours, and the delay of catastrophic growth is about 9 hours. The result of the test with 0.5 mass% PVCap is shown in Figure 5.3. As can be seen, the nucleation time is prolonged by adding 1 vol% of BASF Advanced Polymer to 0.5 mass% of PVCap, although the improvement is not as significant as expected.

Figure 5.5 represents the result of another test with 0.5 mass% of PVCap (1.25 mass% of LUVICAP®) plus 2.5 vol% of BASF Advanced Polymer. Hydrate nucleation
started at 0.5 hours (15.6 °C and 122 bar), which is indicated by the drop of the FFT and amplitude. The initial decline of the system pressure suggested the onset of hydrate formation at 5.2 hours (3.8 °C and 110 bar). The catastrophic growth started at about 20 hours. (Once the catastrophic growth started the outlet was blocked very quickly so that in Figure 5.5a there is no pressure decrease recorded after about 20 hours). In general, the nucleation time is 4.7 hours and the delay of catastrophic growth is about 19 hours. As a consequence of adding a larger quantity of the Advanced Polymer, longer nucleation time and delay of catastrophic growth have been achieved.

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

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

Figure 5.4 Hydrate nucleation and growth in the presence of 0.5 mass% PVCap plus 1 vol% of HYDREAT04-049 (Legend: P=Pressure, T=Temperature, A=Amplitude).
5.4.3 Effect of Molecular Structure of Glycol Ether Compounds

It has been suggested that some members of the glycol ether family are able to improve the performance of kinetic hydrate inhibitors such as PVCap and VC-713 (Cohen J.M., Wolf P.F. and Young W.D., 1998). Our previous investigation, using PVCap and BASF Advanced Polymer at static conditions, has also demonstrated that the synergistic effect of the glycol ether family could prolong nucleation time, delay
Glycol ether can be divided into two series: E series and P series, representing Ethylene and Propylene, respectively. The two series glycol ether compounds may have identical formula but different molecular structures. The E series has a linear structure with a primary hydroxyl, while the major component of the P series has a secondary hydroxyl, with a minor component of a primary hydroxyl with a branched structure. The structural characteristics of the glycol ether used, including molecular formula, molecular structure, and molecular weight, may play a significant role in the synergistic effect.

To understand synergism of glycol ether compounds, i.e., the dependence of synergistic effect of glycol ether compounds on their molecular structures, three members of glycol ether family were chosen and experimentally tested at static conditions. They are Ethylene Glycol Monobutyl Ether (EGME), Ethylene Glycol Diethyl Ether (EGDE), and Propylene Glycol Propyl Ether (PGPE). They have identical molecular formula C₆H₁₄O₂, but different structures:

Ethylene Glycol Monobutyl Ether (EGME): CH₃CH₂CH₂CH₂OCH₂CH₂OH
Ethylene Glycol Diethyl Ether (EGDE): CH₃CH₂OCH₂CH₂OCH₂CH₃
Propylene Glycol Propyl Ether (PGPE): CH₃CH₂CH₂OCH₂CHCH₃

EGME has a linear structure with a primary hydroxyl group, EGDE also has a linear structure without a hydroxyl group, and PGPE has a non-linear structure with a secondary hydroxyl group.

Previously, the effect of PGPE was investigated using both PVCap and BASF Advanced Polymer. In the last six-month period, further tests have been conducted on EGME and EGDE with 0.5 mass% of PVCap (1.25 mass% of LUVICAP®). A concentration 0.75 mass% of the glycol ether compounds was used for all of the chemicals, for comparison.

Figure 5.6 shows the result of the test with 0.5 mass% of PVCap plus 0.75 mass% of EGME under 15 ºC of subcooling. In Figure 5.6a it can be seen that hydrate formation started at 2 hours (4.4 ºC and 111.4 bar), and the catastrophic growth
started at about 30 hours (3.8°C and 98.9 bar). The onset of hydrate nucleation was at 0.5 hours (17°C and 122 bar), which is indicated by the rapid decline of the FFT and amplitude in Figure 5.6b. The nucleation time was 1.5 hours, and the delay of catastrophic growth was about 30 hours.

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

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

Figure 5.6 Hydrate nucleation and growth in the presence of 0.5 mass% PVCap plus 0.75 mass% of EGME (Legend: P=Pressure, T=Temperature, A=Amplitude).

Figure 5.7 shows the result of another test with 0.5 mass% of PVCap plus 0.75 mass% of EGDE under 15°C of subcooling. In Figure 5.7b the rapid drop of the FFT and
amplitude indicates the start point of hydrate nucleation at 0.5 hours (16.7 °C and 121.9 bar), and the onset of hydrate formation at 2 hours (4.9 °C and 111.8 bar). In the test lasting 70 hours, hydrates grew slowly and there was no indication of catastrophic growth according to the system pressure profile. However, the acoustic signal shows that more hydrates grew into liquid phase at around 32 hours and 62 hours, even though the rate of the pressure decline was almost constant.

(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 EGDE (Legend: P=Pressure, T=Temperature, A=Amplitude).
The results of all glycol ether tests are summarised in Table 2. The result of the previous PGPE test is represented in Figure 5.8 to compare the EGME and the EGDE. In Table 2, at static conditions, it seems that PGPE with a non-linear molecular structure and a secondary hydroxyl group not only gave a significantly longer nucleation time, and a delay in catastrophic growth of more than 48 hours, but also effectively hindered natural gas hydrates growing into the liquid phase. The EGME and EGDE in linear molecular structure are not able to significantly alter the nucleation time, regardless if a hydroxyl group is present or absent. However, it is very clear that addition of glycol ether compounds as synergists significantly delay the catastrophic growth in the PVCap-water-natural gas system.

![Figure 5.8](image-url)

Figure 5.8  Hydrate nucleation and growth in the presence of 0.5 mass% PVCap plus 0.75 mass% of PGPE.

<table>
<thead>
<tr>
<th>Glycol ether compounds</th>
<th>Nucleation time /hour</th>
<th>Delay of catastrophic growth /hour</th>
<th>Hydrate quantity in liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGPE</td>
<td>6.6</td>
<td>&gt; 48</td>
<td>Little</td>
</tr>
<tr>
<td>EGME</td>
<td>1.5</td>
<td>30</td>
<td>Large quantity</td>
</tr>
<tr>
<td>EGDE</td>
<td>1.5</td>
<td>&gt;70</td>
<td>Some</td>
</tr>
<tr>
<td>None</td>
<td>1</td>
<td>5</td>
<td>Large quantity</td>
</tr>
</tbody>
</table>

Note: All tests were conducted with 0.5 mass% of PVCap (1.25 mass% of LUVICAP®) plus one of the glycol ether compounds; glycol ether concentration was 0.75 mass%, at static conditions and under 15 °C subcooling.
5.5. SUMMARY

(1) The presence of 1.5 mass% ethylene glycol as a carrier fluid in LUVICAP® does not affect the induction time of PVCap significantly, but results in more hydrates growing into the liquid phase at static conditions. This can be explained by the idea that ethylene glycol prevents a dense hydrate layer from forming at the interface between the gas phase and liquid phase.

(2) Combining PVCap with BASF Advanced Polymer seems to improve the performance of PVCap at static conditions. Addition of HYDREAT 04-049 to LUVICAP® results in longer induction times and a longer delay of catastrophic growth, but it does not prevent gas hydrates from growing into the liquid phase. This result may be another evidence to support previous suggestion, i.e., at static conditions, BASF Advanced Polymer (HYTREAT 04-049) is good at preventing hydrate nucleation rather than hydrate growth.

(3) The comparison in Table 2 shows that the synergistic effect of the glycol ether compounds may be related to their molecular structure, even if they have identical molecular formula, C₆H₁₄O₂ in the tests. Addition of 0.75 mass% of non-linear PGPE with a secondary hydroxyl group to 0.5 mass% of PVCap achieved significantly longer nucleation time (6.6 hours) and delayed catastrophic growth for more than 48 hours, also effectively hindered hydrates growing into the liquid phase. Both EGME and EGDE with a linear structure were not able to make a significant change in nucleation times, 1.5 hours and 1 hour. But it can be concluded that glycol ethers in general can significantly delay the catastrophic growth in the PVCap-water system.

REFERENCES

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 °C to 80 °C

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 °C. 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°C), 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.
Main applications:
1. Evaluating the performance of Kinetic Hydrate Inhibitors (KHI), 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), 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 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.
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 (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 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.
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. Measuring the hydrate stability zone of various fluid systems (e.g., gas, gas condensate and oil systems).
6. Investigating the kinetics of gas hydrate (or wax) formation and dissociation.

Operating conditions:
Pressure: up to 6,000 psia (40 MPa)
Temperature: from –35 to 75 ºC

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 ºC

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 ºC with an accuracy of 0.1ºC. 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 ºC to 80 ºC

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 ºC. 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 0.1ºC. 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 ºC to 80 ºC

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 ºC. 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 °C to 80 °C

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.

CH₄- water
Hydrate formation

CO₂- water
Hydrate formation

CH₄- water
3-phase equilibrium
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.
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 ºC to 80 ºC

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 ºC. 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 overburden 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 0.05ºC. 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 0.01MPa), 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 1MHz. 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 0-90°

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 purpose-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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www.pet.hw.ac.uk/research/hydrate
APPENDIX B

Pressure and Temperature Profiles of the Tests in the Kinetic Rigs
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 1. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap). Testing conditions: 7.3°C and 105 bar, rpm=600rpm. (Run 1)

Figure 2. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap). Testing conditions: 7.8°C and 106 bar, rpm=600rpm. (Run 2)
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 3. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap). Testing conditions: 8.1°C and 106 bar, rpm=600rpm. (Run 3)

Figure 4. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap). Testing conditions: 8.3°C and 107 bar, rpm=600rpm. (Run 4)

B.3
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 5. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap)-0.75% PGPE. Testing conditions: 7.6°C and 101 bar, rpm=600rpm. (Run 1)

Figure 6. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap)-0.75% PGPE. Testing conditions: 6.6°C and 100 bar, rpm=600rpm. (Run 2)
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 7. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap)-0.75% PGPE. Testing conditions: 6.8°C and 100 bar, rpm=600rpm. (Run 3)

Figure 8. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap)-0.75% PGPE. Testing conditions: 7.4°C and 101 bar, rpm=600rpm. (Run 4)
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 9. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap)-1.5% PGPE. Testing conditions: 7.3°C and 101 bar, rpm=600rpm. (Run 1)

Figure 10. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap)-1.5% PGPE. Testing conditions: 7.9°C and 101 bar, rpm=600rpm. (Run 2)
Figure 11. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap)-1.5% PGPE. Testing conditions: 7.9°C and 101 bar, rpm=600rpm. (Run 3)

Figure 12. Pressure and temperature profiles for NG-water-1%PVCap (Luvicap)-1.5% PGPE. Testing conditions: 8.4°C and 102 bar, rpm=600rpm. (Run )
Figure 13. Pressure and temperature profiles for NG-water-1%PVCap (Luviskol). Testing conditions: 7.2°C and 93 bar, rpm=600rpm. (Run 1)

Figure 14. Pressure and temperature profiles for NG-water-1%PVCap (Luviskol). Testing conditions: 7.1°C and 92 bar, rpm=600rpm. (Run 2)
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 15. Pressure and temperature profiles for NG-water-1%PVCap (Luviskol). Testing conditions: 7.3°C and 92 bar, rpm=600rpm. (Run 3)

Figure 16. Pressure and temperature profiles for NG-water-1%PVCap (Luviskol). Testing conditions: 8.0°C and 93 bar, rpm=600rpm. (Run 4)
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 17. Pressure and temperature profiles for NG-water-1%PVCap (Luviskol)-0.75%PGPE. Testing conditions: 5.5°C and 89 bar, rpm=600rpm. (Run 1)

Figure 18. Pressure and temperature profiles for NG-water-1%PVCap (Luviskol)-0.75%PGPE. Testing conditions: 5.7°C and 89 bar, rpm=600rpm. (Run 2)
Figure 19. Pressure and temperature profiles for NG-water-1%PVCap (Luviskol)-0.75%PGPE. Testing conditions: 5.7°C and 89 bar, rpm=600rpm. (Run 3)

Figure 20. Pressure and temperature profiles for NG-water-1%PVCap (Luviskol)-0.75%PGPE. Testing conditions: 6.2°C and 90 bar, rpm=600rpm. (Run 4)
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 21. Pressure and temperature profiles for NG-water-1%PVCap (Lubasin). Testing conditions: 9.0°C and 92 bar, rpm=600rpm. (Run 1)

Figure 22. Pressure and temperature profiles for NG-water-1%PVCap (Lubasin). Testing conditions: 8.9°C and 92 bar, rpm=600rpm. (Run 2)
Figure 23. Pressure and temperature profiles for NG-water-1%PVCap (Lubasin). Testing conditions: 9.3°C and 93 bar, rpm=600rpm. (Run 3)

Figure 24. Pressure and temperature profiles for NG-water-1%PVCap (Lubasin). Testing conditions: 9.3°C and 93 bar, rpm=600rpm. (Run 4)
Figure 25. Pressure and temperature profiles for NG-water-1%PVCap (Lubasin)-0.75% PGPE. Testing conditions: 8.3°C and 99 bar, rpm=600. (Run 1)

Figure 26. Pressure and temperature profiles for NG-water-1%PVCap (Lubasin)-0.75% PGPE. Testing conditions: 9.2°C and 100 bar, rpm=600. (Run 2)
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 27. Pressure and temperature profiles for NG-water-1%PVCap (Lubasin)-0.75% PGPE. Testing conditions: 8.8°C and 100 bar, rpm=600. (Run 3)

Figure 28. Pressure and temperature profiles for NG-water-1%PVCap (Lubasin)-0.75% PGPE. Testing conditions: 9.3°C and 93 bar, rpm=600. (Run 4)
Figure 29. Pressure and temperature profiles for NG-water –0.5mass% PVCap. Testing conditions: 5.5 °C and 102 bar, kinetic rig 2, rpm=600.

Figure 30. Pressure and temperature profiles for NG-water –0.5mass% PVCap. Testing conditions: 5.5 °C and 102 bar, kinetic rig 2, rpm=600.
Figure 31. Pressure and temperature profiles for NG-water –0.5mass% PVCap-2.5 vol% HYTREAT® 04-049. Testing conditions: 5.3 °C and 101 bar, kinetic rig 2, rpm=600.

Figure 32. Pressure and temperature profiles for NG-water –0.5mass% PVCap-2.5 vol% HYTREAT® 04-049. Testing conditions: 5.3 °C and 101 bar, kinetic rig 2, rpm=600.
Figure 33. Pressure and temperature profiles for NG-water –0.5mass% PVCap-2.5 vol% HYTREAT® 04-049. Testing conditions: 4.8 °C and 100 bar, kinetic rig 2, rpm=600.

Figure 34. Pressure and temperature profiles for NG-water –0.5mass% PVCap-2.5 vol% HYTREAT® 04-049. Testing conditions: 4.8 °C and 100 bar, kinetic rig 2, rpm=600.
Figure 35. Pressure and temperature profiles for NG-water –1mass% PVCap(no solvent). Testing conditions: 5 °C and 101 bar, kinetic rig 5, rpm=600.

Figure 36. Pressure and temperature profiles for NG-water –1mass% PVCap(no solvent). Testing conditions: 4.8 °C and 100 bar, kinetic rig 5, rpm=600.
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 37. Pressure and temperature profiles for NG-water –1mass% PVCap(no solvent). Testing conditions: 5 °C and 100 bar, kinetic rig 5, rpm=600.

Figure 38. Pressure and temperature profiles for NG-water –1mass% PVCap-1.5 mass% ethylene glycol. Testing conditions: 5.2 °C and 100 bar, kinetic rig 5, rpm=600.
Figure 39. Pressure and temperature profiles for NG-water –1mass% PVCap-1.5 mass% ethylene glycol. Testing conditions: 4.9 °C and 100 bar, kinetic rig 5, rpm=600.

Figure 40. Pressure and temperature profiles for NG-water –1mass% PVCap-20 mass% ethylene glycol. Testing conditions: -1.5 °C and 90 bar, kinetic rig 1, rpm=600.
Figure 41. Pressure and temperature profiles for NG-water –1mass% PVCap-20 mass% ethylene glycol. Testing conditions: -1.3 °C and 95 bar, kinetic rig 1, rpm=600.

Figure 42. Pressure and temperature profiles for NG-water –1mass% PVCap-20 mass% ethylene glycol. Testing conditions: -3 °C and 92 bar, kinetic rig 1, rpm=600.
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 43. Pressure and temperature profiles for NG-water –1mass% PVCap-20 mass% ethylene glycol. Testing conditions: -3.2 °C and 90 bar, kinetic rig 1, rpm=600.

Figure 44. Pressure and temperature profiles for NG-water –1mass% PVCap-20 mass% ethylene glycol. Testing conditions: -3.3 °C and 96 bar, kinetic rig 1, rpm=600.
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 45. Pressure and temperature profiles for NG-water –1mass% PVCap-20 mass% ethylene glycol. Testing conditions: -3.4 °C and 94 bar, kinetic rig 1, rpm=600.

Figure 46. Pressure and temperature profiles for NG-water –1mass% PVCap. Testing conditions: 4.2 °C and 90 bar, kinetic rig 1, rpm=600.
Figure 47. Pressure and temperature profiles for NG-water –1mass% PVCap. Testing conditions: 4.2 °C and 93 bar, kinetic rig 1, rpm=600.

Figure 48. Pressure, temperature and torque profiles for NG-Condensate-Water system with W/C=0.33 in kinetic rig 5, helical tube mixer, rpm=400.
Figure 49. Pressure, temperature and torque profiles for NG-Condensate-Water system in the presence of 0.5 mass% AA (HT04-106) in water phase. W/C=0.33, kinetic rig 5, helical tube mixer, rpm=400.
APPENDIX C

Summary of Synergists Described in Patents
Table 1. Summary of synergists described in patents.

<table>
<thead>
<tr>
<th>Type</th>
<th>Examples</th>
<th>Performance</th>
<th>Ref. (US Pat. No.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion Inhibitors</td>
<td>Primary, secondary or tertiary amines or a quaternary ammonium salt with at least one hydrophobic group e.g. benzyl, lauryl, or dodecyl substituted ammonium halides.</td>
<td>From Duncum et al US 6,439,877: Pressured rig with water and methane at 70 bar and 4°C (stirred). Test shows the effect of various corrosion inhibitors. The best is alkyl benzyl dimethylammonium (500ppm) with tetrapentylammonium bromide (1000ppm), VP:VCap:VIMA co-polymer (1000ppm), which had an induction time of 2039 minutes. Successful field tests were also carried out in the North Sea, using similar compounds as above but in higher concentrations (with mono butyl ethylene glycol ether).</td>
<td>6,439,877 (6,319,971)</td>
</tr>
<tr>
<td>Alcoholic &amp; Glycolic Solvents</td>
<td>Methanol, ethanol, isopropanol, butanol (6,096,816), 2-butoxy ethanol (6,186,699; 6,451,891), 2-propoxy ethanol, ethylene glycol, propylene glycol (5,723,524), and 2-isobutoxyethanol (6,177,497).</td>
<td>No data on synergism. From Klug et al US 6,177,497: describes the only patent issued as an actual “synergist”.</td>
<td>6,096,816 6,177,497 6,186,699 5,723,524 (6,319,971)</td>
</tr>
<tr>
<td>Quaternaryonium salts</td>
<td>Tetra alkyl onium salts e.g. TBAB</td>
<td>From Kelland et al US 6,319,971: The use of TBAB as a synergist is explored, however the results of a high pressure stirred vessel are inconclusive, though TBAB seems to effect induction time of the KHI.</td>
<td>H1 749 (6,319,971)</td>
</tr>
<tr>
<td>Triamine oxides</td>
<td>Mono-, di-, or tri-alkylamine oxides</td>
<td>No data on synergism</td>
<td>(6,319,971)</td>
</tr>
<tr>
<td>Surface active ingredients</td>
<td>Na C4 Sulphate, Na C4 Sulphonate, Na C4 Sulphonate</td>
<td>From Colle et al H1 749: A stop ball, THF test was carried out with various KHI and surface active compounds (see left). These chemicals seem to considerably enhance performance. Varies with different chemicals. The most notable being 0.5% PMAM inhibited the system for 41 minutes, and 2% Na C4 Sulphate inhibited for 15 minutes; but together the overall inhibition was over 3885 minutes.</td>
<td>H1 749</td>
</tr>
<tr>
<td>Co-synergism between KHI</td>
<td>Index developed in Kelland et al US 6,319,971</td>
<td></td>
<td>6,319,971</td>
</tr>
</tbody>
</table>