Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors

September 2002-August 2005 Programme
Low Dosage Hydrate Inhibitors

- Generally, based on trial and error
- Limitations of the existing LDHIs

- Projects that contributed to this proposal
  - *Gas hydrates in subsea sediments (glass micromodel)*
  - *Rational design and testing of low dosage hydrate inhibitors (kinetic rig + torque measurement)*
Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors

• Objectives:
  – Better understanding of gas hydrate formation in various fluid systems
  – Investigating the mechanism of gas hydrate inhibition offered by LDHIs
  – Evaluating a number of existing LDHIs (basic compounds and commercial formulations)
  – Improving the design and/or deployment of LDHI

• Methodology
  – Integrated micro and macro-scale study
Deliverables

- Data on gas hydrate nucleation and growth
- Novel data on the mechanism of gas hydrate inhibition by LDHIs
- Data on the induction time, rate of hydrate growth, rheological properties
- Effect of LDHIs on the kinetics and transportability of gas hydrates
Deliverables

• Information on validation and repeatability of micromodel tests in bulk conditions

• Information on hydrate crystal particle size and distribution

• Guidelines on effective design and deployment of LDHIs

• Guidelines on screening of potential LDHIs
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- **Experimental Equipment**
  - Glass Micromodel
    - Medium and high pressure (80-400 bar)
  - Kinetic rig
    - Rigs 1 to 4 (300 to 700 bar)

- **New Tools**
  - Visual rig (500 bar)
  - Ultrasonic (400 bar)

- **Under construction**
  - Kinetic rig with helical mixer (should be ready within 1 month)
  - Visual kinetic rig (should be ready within 2 months)
  - New ultrasonic rig (should be ready within 3 months)
  - Visual kinetic/micromodel/ultrasonic rig (should be ready within 4 months)
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- Kinetic Rigs
  - 300 to 700 bar, P, T and Torque measurements
Kinetic Rig Experiments

- Progress in the last six months
  - *Testing the new KHIs:*
    - (HI03-22), (HI03-24), (HI03-187)
    - Methane and natural gas
    - Effect of degree of subcooling
    - Flowing and shut-in conditions
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- **Micromodel Rigs**
  - 400 bar, -25 to 50 °C
  - 0-90° Rotation
  - Various flow conduits
Micromodel Rigs Experiments

• Progress in the last six months
  – Investigating gas hydrate formation/growth and morphology in the presence of:
    (HI03-22), (HI03-24), (HI03-187)
      – Natural gas
      – Methane
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- Visual Rig (designed for wax and wax-hydrate studies)
Visual Rig Experiments

- Progress in the last six months
  - **Hydrate formation from:**
    - Natural gas-water–hydrocarbon liquid (decane / separator condensate) in the presence and absence of PVCAP
  
  - **Interfacial Tension Measurements using pendant drop method:**
    - methane–water
    - methane–water-1.5 mass% ethylene glycol
    - methane–water-1.5 mass% ethylene glycol–1% Pvcap
    - methane – octane - water
    - methane – octane - water- AA (HI03-186)
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• Ultrasonic (designed for gas hydrates in sediments)
Ultrasonic Rig Experiments

- Progress in the last six months
  - Hydrate formation in
    - Natural gas-water system in the presence of:
    - PVCAP
    - PVCAP + Synergist (TBAB)
    - New KHI (HI03-22)
Anti-Agglomerant LDHI

• Progress in the last six months
  – *Gas hydrate formation in a condensate system (octane) with and without AA (HI03-186)*
    – In the glass micromodel rig
    – Examining the performance of kinetic rig for evaluating AAs
Flow Assurance: Micro and Macro-Scale Evaluation of LDHI

KINETIC RIG EXPERIMENTS

Mosayyeb (Jahan) Arjmandi
Objectives of Experiments in Kinetics Rig

Evaluating the performance of the new formulations of kinetic inhibitors:

- HI03-22 (PVCAP, EG, Water, synergist chemical)
- HI03-24 (PVCAP, EG, Water, same synergist chemical as HI03-22 with different ratio)
- HT03-187 (PVCAP, EG, Water, different synergist chemical from that used in the above two inhibitors)

in bulk conditions (5 volume% in water) in different systems:

- Methane
- Natural Gas

and in different conditions:

- Different degrees of subcooling
- Mixing and Static conditions
Schematic Diagram of the Hydrate Kinetics Rig-1

- Pressure transducer
- Coolant Jacket
- Inlet/outlet
- Temperature probe
- Magnetic motor
- PC interface
- Stirrer blade

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Project Steering Committee Meeting, June 2004
### Natural Gas Phase Boundary and Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
<th>i-Butane</th>
<th>n-Butane</th>
<th>i-Pentane</th>
<th>Nitrogen</th>
<th>Carbon dioxide</th>
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<tbody>
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<td>0.1</td>
<td>3.24</td>
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**Graph:**

- **Methane**
- **Natural Gas**

Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors.
Project Steering Committee Meeting, June 2004
### NG - Water – HI03-24 (5vol%)

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
<th>Subcooling</th>
<th>Induction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>3.9 / 107.5</td>
<td>15</td>
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<td>2</td>
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<td>14.8</td>
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<td>600</td>
<td>5.2 / 127.9</td>
<td>14.6</td>
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<td>600</td>
<td>4.0 / 95</td>
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<td>600</td>
<td>3.8 / 89.5</td>
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<td>4.0 / 90</td>
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<td>10</td>
<td>0</td>
<td>4.4 / 95</td>
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<td>20</td>
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<tr>
<td>11</td>
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<td>4.2 / 90</td>
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<td>12</td>
<td>600</td>
<td>5.3 / 108.9</td>
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<td>15</td>
<td>600</td>
<td>4.5 / 90</td>
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<tr>
<td>16</td>
<td>600</td>
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<tr>
<td>17</td>
<td>600</td>
<td>5.2 / 94.7</td>
<td>13.0</td>
<td>&gt;30</td>
</tr>
</tbody>
</table>

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*Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors.*  
*Project Steering Committee Meeting, June 2004*
NG-Water – HI03-24 (5vol%), Mixing Effect

![Graph showing the effect of mixing on hydrate formation in NG-Water with HI03-24 (5vol%)](image)

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Effect of Hydrate Structure on the Performance of PVCAP

Materials:

2.5 mass % Luvicap® in water

C₁(97 mol%) - C₃(3 mol%) Gas mixture sII Hydrate

C₁(68.6 mol%) - C₂(31.4 mol%) Gas mixture sI Hydrate
Hydrate Phase Boundaries of the Gas Mixtures

- C1(97%)-C3(3%)
- C1(68.6%)-C2(31.4%)

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Project Steering Committee Meeting, June 2004
### Summary of the Tests on Gas Mixtures

#### Results of the Tests on C1-C3 sII Hydrate

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
<th>Subcooling</th>
<th>Induction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>°C / bar / °C</td>
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<td>Time / hrs</td>
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<td>2</td>
<td>1000</td>
<td>0.8 / 97 / 18</td>
<td>26</td>
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<td>3</td>
<td>1000</td>
<td>0.2 / 97 / 18.6</td>
<td>16</td>
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</table>

#### Results of the Tests on C1-C2 sI Hydrate

<table>
<thead>
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<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
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<th>Induction</th>
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<td></td>
<td>°C / bar / °C</td>
<td></td>
<td>Time / hrs</td>
</tr>
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<td>1000</td>
<td>1.9 / 96.9 / 17.1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>3.8 / 97.2 / 15.2</td>
<td>0</td>
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</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>4.2 / 97.2 / 14.8</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>4.2 / 97.2 / 14.8</td>
<td>1.5</td>
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</tbody>
</table>

**Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors.**

*Project Steering Committee Meeting, June 2004*
## Methane – Water- HI03-24 (5 vol%) 

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
<th>Subcooling</th>
<th>Induction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>°C / bar</td>
<td>°C</td>
<td>time/hrs</td>
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<td>1</td>
<td>600</td>
<td>4.9 / 119</td>
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<td>3.5</td>
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<td>8.5</td>
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<td>3</td>
<td>600</td>
<td>5.2 / 119.3</td>
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<td>10</td>
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<td>5.3 / 120</td>
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<tr>
<td>6</td>
<td>0</td>
<td>5.2 / 120</td>
<td>9.3</td>
<td>20</td>
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</table>
Methane - Water – HI03-24 (5vol%) Mixing Effect

Subcooling 9.3 °C, No mixing
Subcooling 9.3 °C, 600rpm
Subcooling 9.6 °C, 600rpm
<table>
<thead>
<tr>
<th>Test No.</th>
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<th>Subcooling °C</th>
<th>Induction Time / hrs</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>4.5 / 93.5</td>
<td>13.5</td>
<td>1</td>
</tr>
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<td>3.7 / 65</td>
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<td>3.7</td>
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<td>600</td>
<td>3.8 / 65</td>
<td>11.9</td>
<td>4.5</td>
</tr>
<tr>
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<td>600</td>
<td>3.8 / 65</td>
<td>11.9</td>
<td>6</td>
</tr>
<tr>
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<td>600</td>
<td>3.9 / 65</td>
<td>11.8</td>
<td>5.7</td>
</tr>
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<td>7</td>
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<td>4.0 / 64.8</td>
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<tr>
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<td>4.0 / 65.5</td>
<td>11.7</td>
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<td>4.0 / 65.5</td>
<td>11.7</td>
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<td>Test No.</td>
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<td>Testing T/P</td>
<td>Subcooling</td>
<td>Induction</td>
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<td>°C</td>
<td>time/hrs</td>
</tr>
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<td>4.8 / 100</td>
<td>13.7</td>
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<td>600</td>
<td>5.0 / 100</td>
<td>13.5</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>4.7 / 96.6</td>
<td>13.4</td>
<td>&gt;10</td>
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<td>600</td>
<td>5.2 / 97.2</td>
<td>13.1</td>
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### NG-Water – HI03-22

**Inhibitor Concentration vs. Subcooling**

<table>
<thead>
<tr>
<th>HI03-22</th>
<th>Subcooling *</th>
</tr>
</thead>
<tbody>
<tr>
<td>vol%</td>
<td>°C</td>
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<td>2</td>
<td>10.9</td>
</tr>
<tr>
<td>5</td>
<td>13.1</td>
</tr>
</tbody>
</table>

* Maximum degree of subcooling that inhibitor can prevent hydrate for more than one day
<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
<th>Subcooling</th>
<th>Induction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600</td>
<td>4.8 / 99.8</td>
<td>13.7</td>
<td>&gt;52</td>
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<td>&gt;75</td>
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<td>-0.1 / 95</td>
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<tr>
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<td>0</td>
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<td>&gt;56</td>
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</tbody>
</table>
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Project Steering Committee Meeting, June 2004

NG-Water- HT03-187 (5VOL%)

Chemical: NG-Water- HT03-187 (5VOL%)

Nomixing, 18.8 °C Subcooling
Mixing, 18.4 °C Subcooling
Comparison of KIs in NG-Water System

- HT03-187 (13.7 °C subcooling)
- Luvicap 13.9 °C
- HI-0322 13.7 °C
- HI-0324 13.7 °C
### Methane-Water- HT03-187 (5VOL%)

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
<th>Subcooling</th>
<th>Induction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>1.8 / 114.5</td>
<td>12.4</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>2.3 / 114.4</td>
<td>11.9</td>
<td>9</td>
</tr>
<tr>
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<td>2.3 / 114.4</td>
<td>11.9</td>
<td>&gt;60</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>2.1 / 114.5</td>
<td>12.1</td>
<td>&gt;60</td>
</tr>
</tbody>
</table>

### Luvicap ® 2.5 mass% [Pvcap 1mass%]

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
<th>Subcooling</th>
<th>Induction</th>
</tr>
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<tr>
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<td>4.5 / 118</td>
<td>10</td>
<td>5</td>
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</table>
### Methane – Water- HI03-24 (5 vol%) 

<table>
<thead>
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<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
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<th>Induction</th>
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</thead>
<tbody>
<tr>
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<td>°C / bar</td>
<td>°C</td>
<td>time/hrs</td>
</tr>
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<td>1</td>
<td>600</td>
<td>4.9 / 119</td>
<td>9.6</td>
<td>3.5</td>
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<tr>
<td>2</td>
<td>600</td>
<td>5.2 / 119.4</td>
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<td>8.5</td>
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<td>0</td>
<td>5.2 / 120</td>
<td>9.3</td>
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</tbody>
</table>
Summary

- Three new formulations of PVCAP based kinetic inhibitors were tested in different gas systems and at various conditions.

- The maximum degree of subcooling in which the above inhibitors (5vol%) can prevent hydrates for more than one day in natural gas water system were found to be 13.3 °C, 13.1 °C and > 18.4 °C for HI03-24, HI03-22 and HT03-187 respectively.
Summary

- From the results of the tests it appeared that the performance of HT03-187 in natural gas – water system and methane – water system is better than the other two and Luvicap®.

- The inhibitors tested in general performed better in natural gas system than methane system.

- For the mentioned inhibitors tested in natural gas-water system, at the same conditions, the induction times at static conditions were found to be more than those of mixing conditions.
Flow Assurance:
Micro and Macro-Scale Evaluation of LDHI

Testing the New Anti-Agglomerant

Mosayyeb (Jahan) Arjmandi

Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors. Project Steering Committee Meeting, June 2004
Objectives of Experiments in Kinetics Rig

Evaluating the performance of the new Anti-Aggglomerant HT03-186 (2.5 volume% in water) in natural gas – water- condensate system in:

- **Kinetic Rig**

- **MicroModel set-up**
## Materials

### Natural Gas:

<table>
<thead>
<tr>
<th>Component</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
<th>i-Butane</th>
<th>n-Butane</th>
<th>i-Pentane</th>
<th>Nitrogen</th>
<th>Carbon dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol%</td>
<td>87.32</td>
<td>5.67</td>
<td>1.68</td>
<td>0.23</td>
<td>0.4</td>
<td>0.1</td>
<td>3.24</td>
<td>1.36</td>
</tr>
</tbody>
</table>

- East Firgg Field Condensate
- Distilled Water
- Anti-Agglomemerant HT03-186

* In the tests an emulsion of W/C=0.33 was used
Natural Gas-Water Blank Test

Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors.  
Project Steering Committee Meeting, June 2004
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Project Steering Committee Meeting, June 2004
Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors.

Project Steering Committee Meeting, June 2004

Natural Gas – Water – 2.5 vol% HT03-186
Shut-in – Restart Case
Condensate-Water-NG

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Project Steering Committee Meeting, June 2004
Condensate-Water-NG-AA

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Project Steering Committee Meeting, June 2004
Condensate-Water-NG-AA

Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors.
Project Steering Committee Meeting, June 2004
Condensate-Water-NG-AA

Video 1
Flow Assurance: Micro and Macro-Scale Evaluation of LDHI

KINETIC AND VISUAL OBSERVATIONS OF NATURAL GAS HYDRATE FORMATION IN STATIC CONDITIONS

INTERFACIAL TENSION MEASUREMENTS

Rod Burgass
Outline of Presentation

• Kinetic and visual observations of formation of natural gas hydrates in the presence of
  - 2.5 mass% LUVICAP® with decane
  - 2.5 mass% LUVICAP® with separator condensate
  - 5 Volume% HT03-187®

• Interfacial measurements
  - Liquid water/liquid hydrocarbon in water/octane/methane system
  - Liquid water/liquid hydrocarbon in water/octane/methane system with 1 volume% HT03-186® present in water
Schematic of high pressure (512 bar) visual rig
Plot of pressure and time data for two tests with decane/natural gas and water without and with 2.5 mass% LUVICAP®

- T=35°C
- T=4°C

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Picture showing hydrate crystals, formed from natural gas, forming into the liquid water phase from the water/liquid hydrocarbon interface.
Picture showing hair-like hydrates, formed from natural gas growing from the cell walls into the vapour phase
Plot of pressure and time data for three tests with decane/natural gas and water without and with 2.5 mass% LUVICAP®

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Plot of pressure and time data for two tests with separator condensate/natural gas and water without and with 2.5 mass% LUVICAP®
Comparison of pressure/time data for three tests with natural gas and 2.5 mass% LUVICAP® present in the water

- **T=35°C**
- **T=4°C**

- **No liquid hydrocarbon**
- **10cc decane**
- **10cc separator condensate**
Comparison of pressure and time data for tests with natural gas with 2.5 mass% LUVICAP® and 5 volume% HT03-187®

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IFT Measurements by pendant drop method

Dropper width
0.45 mm
IFT MEASUREMENT BY PENDANT DROP METHOD

$$IFT = \frac{\Delta \rho \cdot g \cdot d_e^2}{H}$$

$\Delta \rho$  difference in density between phases  

$g$  gravity constant  

$H$  shape factor obtained from look-up tables based upon ratio of $d_s/d_e$
Experimental IFT measurements for methane and water at 37.8°C, using pendant drop method, from this work compared with literature data and data measured earlier at HWU.
Experimental IFT measurements between aqueous and vapour phases for methane/water and methane/aqueous solutions of ethylene glycol 1.5 mass% and LUVICAP® 2.5 mass% at 10°C.
IFT values for 1 volume% HT 03-186® aqueous solution/liquid hydrocarbon in the methane/octane/1 volume% HT03-186® aqueous solution system at different pressures and temperatures.
Comparison of IFT measurements without and with HT 03-186® at 10.7°C

Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors. Project Steering Committee Meeting, July 2003
Hydrate Nucleation Tests Using Ultrasonic Waves

in the presence of PVCAP/TBAB/HI03-22

By Jinhai Yang
Hydrate Nucleation Tests Using Ultrasonic Waves

- Objectives
- Results
- Summary
1 Objectives

Previous Investigation

❖ System:

Natural gas
Carbon dioxide + Distilled water + 1 mass% of PVCAP
THF

❖ Main conclusion:

PVCAP prolongs the induction time of hydrate formation through not only delaying the catastrophic growth but also slowing down hydrate nucleation, but mainly inhibiting hydrate growth.
1 Objectives

Objectives:

- Investigate the effect of TBAB as a synergist on NG hydrate nucleation and growth.
- Experimentally examine how a kinetic inhibitor (HI03-22) acts to delay NG hydrate nucleation and growth, compared with PVCAP tests.
1 Objectives

Test Conditions

- Bulk liquid and gas phases without mixing

71 volume% of liquid phase and 29 volume% of gas phase in the test cell
1 Objectives

Test Conditions

- Bulk and static condition
- Hydrate former: a natural gas
- T and P Control: 122 bar at 20 °C → 4 °C

The phase boundary of the NG hydrates
2 Results

2.0 Review of acoustic response in the previous NG test in the absence of any additives

No time gap between nucleation and growth.

Pressure profile could not show hydrate formation.

FFT and amplitude simultaneously indicated that NG hydrates started forming at 58 min (133.2 bar and 13.1 °C), significant growth finished in 120 minutes.

Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors. Project Steering Committee Meeting, June 2004
2.1 Effect of TBAB as a synergist

- In the presence of 0.5 mass% of PVCAP

Ultrasonic wave showed that the nucleation started at 30 min (17 °C, 121 bar).

Pressure declining showed hydrates started formation at 250 min (4 °C, 110 bar).

Outlines of Pressure and ultrasonic wave: catastrophic growth started at 430 min (4 °C, 109 bar), after 3 hours from the onset of hydrates formation.
2.1 Effect of TBAB as a synergist

- In the presence of 0.5 mass% of PVCAP and 0.5 mass% of TBAB (Tetrabutylammonium bromide)

FFT and amplitude showed nucleation at 30 min (16 °C, 121 bar).

Pressure declining indicated the onset of hydrate formation at 210 min (4 °C, 110 bar).

P/T and ultrasonic signals responded catastrophic growth at 250 min, 40 min later from the onset.
2.1 Effect of TBAB as a synergist

0.5 mass% of PVCAP + 0.5 mass% of TBAB

Delay of nucleation: about 3-4 hours, no significant difference.

Delay of catastrophic growth: 3 hours for 0.5 mass% of PVCAP only, less than 1 hour for 0.5 mass% of PVCAP and 0.5 mass% of TBAB.

Rate of hydrate growth (in the first 12 hour from the onset): 0.6 bar/hour for PVCAP test, 2.4 bar/hour for PVCAP + TBAB test.
2.2 Comparison of PVCAP with HI03-22

In the presence of 5 vol% of HI03-22 (equivalent to 1 mass% of PVCAP)

FFT showed nucleation started at 25 min, more obviously at 70 min.

It was hard to tell where hydrate formation started because of too tiny pressure drop, about 1 bar of pressure drop in the first 12 after the temperature became constant.

Profiles of Pressure, amplitude and FFT showed that the catastrophic growth started at least 47 hours after the onset of growth.
2.2 Comparison of PVCAP with HI03-22

- In the presence of 1 mass% of PVCAP

FFT showed nucleation at 50 min.

Pressure drop showed the onset of hydrates formation at about 160 min.

Pressure drop clearly indicated the catastrophic growth after 38 hour from the onset.

Pressure declined by 7 bar in the first 12 hours after the onset of hydrate growth.
2.2 Comparison of PVCAP with HI03-22

Both PVCAP and HI03-22 significantly delay the catastrophic growth of NG hydrates: 38 hours for 1 mass% of PVCAP, 47 hours for the equivalent 5 vol% of HI03-22.

Relatively, HI03-22 seems to more effectively control nucleation/the very beginning of hydrate formation than PVCAP did.

Catastrophic growth happened more suddenly in PVCAP test than in HI03-22 test.
3 Summary --- under static conditions

1 Effect of TBAB as a Synergist
   - Shortening the delay of catastrophic growth of NG hydrates.
   - No significant difference between nucleation delay of NG hydrates.

Addition of TBAB as a synergist to PVCAP may weaken the effectiveness of PVCAP under static condition.

2 Comparison of PVCAP with HI03-22
   - Both PVCAP and HI03-22 significantly delay the catastrophic growth of NG hydrates.
   - HI03-22 seems to more effectively control nucleation/the very beginning of hydrate formation than PVCAP did under static condition.
   - Catastrophic growth happened more suddenly with PVCAP than with HI03-22.

Addition of suitable synergists in a right way may improve the performance of base polymers as kinetic hydrate inhibitors.
Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors

Visual observation by Micromodel Experiments

Zahidah Md Zain
Objectives

- Visual observation on mechanism of hydrate formation and growth
- Effect of inhibitors on hydrate crystal morphology
- Effect of inhibitors on morphology for different hydrate structure (sI and sII)
  - Fluid systems:
    - Natural gas - water
    - Methane - water
  - LDHI:
    - HI03-22
    - HI03-24
    - HT03-187
HP Micromodel Set-up

Operating condition:
Pressure: up to 6000 psia (400 bar)
Temperature: -20 °C to 80 °C
Hydrate formation: NG-Water System + HI03-22
1360 psia/94 bar, 17°C subcooling

- Before hydrate formation
- 1 hr after hydrate formation
- 47 hrs after hydrate formation

- At 4.3°C (14°C subcooling), no hydrate formation after 24 hrs. Hydrate formed at 0.5°C (17°C subcooling).
- Initial formation at gas-water interface moving inside gas bubbles as forming non-transparent masses of hydrate layer. No formation in water phase.
- Thin patches of flaky hydrate crystals

HI03-22 (PVCAP with synergist) more effective in delaying hydrate formation compared to Luvicap® (PVCAP without synergist*) at static condition

* Luvicap® (14°C subcooling with 8 hrs induction time)
Hydrate formation: NG-water System + HI03-24
1500 psia/103 bar, 11.4°C subcooling

Different degrees of subcooling lead to different mechanism of hydrate formation and morphologies.

- **(a) Before hydrate formation**
- **(b) 3 hr after hydrate formation**
- **(c) 34 hrs after hydrate formation**

- Formed immediately after reached 7.1°C (11.4°C subcooling)
- Hydrate formation via dissolution of gas into the water phase.
- Smooth whiskery hydrate crystal (water phase) and threadlike hydrate (gas phase)
Video footage: NG-water System + HI03-24
1500 psia/103 bar, (11.4°C subcooling), real time footage
Hydrate formation: NG-Water System + HI03-24

- Different degrees of subcooling → different mechanism of hydrate formation & morphologies.
- HI03-24 not effective in preventing hydrate formation in water phase.

(a) Before hydrate formation

(b) 24 hr after hydrate formation

(c) 40 hrs after hydrate formation

1500 psia/103 bar, (12.4°C subcooling)

W G H

- Non transparent hydrate in water phase
- Small dendrite & round shape hydrate in gas phase

1350 psia/93 bar, (14.4°C subcooling)

G W H

- Circular & thin patches of crystal flake in gas phase
Video footage: NG-water System + HI03-24
1500 psia/103 bar, (12.4°C subcooling), 900x real time

Video 3
Video footage: NG-water System + HI03-24
1350 psia/93 bar, (14.4°C subcooling), 120x real time

Video 4
Effect of Inhibitors on Hydrate Crystal Morphology
Natural gas hydrate (14°C subcooling)

- Blank & Lucicap®: No significant differences
- HI03-24: patches of very thin crystal flakes
- HI03-22: small hydrate particles

Synergist chemicals have effect on hydrate morphology and particle size for the same system.
Effect of Inhibitors on Hydrate Growth
Natural gas hydrate (14°C subcooling)

- Basis for crystal growth: conversion of hydrate particles to more oriented crystals
  - Luvicap® - hydrate growth continue
  - HI03-22 - final stage of hydrate structure formation
  - HI03-24 - growth terminate

The most effective in slowing down the hydrate crystal growth:
Luvicap® > HI03-22 > HI03-24
Hydrate formation: CH₄-Water System + HI03-24
1700 psia/117 bar, (11.5°C subcooling)

- Hydrate formed at 3°C (11.5°C subcooling)
- Growth initiated in the gas bubbles profile in the form of grey layer with thick interface.
- Thick and rough hydrate crystals separated within original gas profiles.
Effect of Inhibitors on morphology for different hydrate Structure

With HI03-22 (10°C subcooling):
- NG-water (sII): patches of very thin crystal flakes
- CH4-water (sI): continuous thin solid crystals

With HI03-24 (11.4°C subcooling):
- NG-water (sII): whiskery and tread like crystals
- CH4-water (sI): thick and rough crystals

Synergist chemicals have effect on hydrate morphology for different hydrate structure
Hydrate formation: NG-Water System + HT03-187
1300 psia/90 bar, (13.9°C subcooling)

- Hydrate formed at 4°C after 80 hours of induction time. No formation in water phase.

- Thin patches of hydrate crystals with snowy and flake type morphology. A more porous hydrate, less packed and with disorder in the structure leading to higher porosity
Hydrate formation: CH4-Water System + HT03-187
1700 psia/117 bar, (13.6°C subcooling)

- Hydrate formed at 0.7°C after reducing temperature from 4.3°C within 92 hours.
  No formation in water phase.
- Form shells inside the gas bubble profile and water remain in the middle.
Effect of different synergist chemical on Hydrate Crystal Morphology
Natural gas hydrate (14°C subcooling)

Significant different on hydrate morphology for different synergist chemical

thin patches of snowy crystal flakes
continuous hydrate crystals
Summary of results

- HI03-22 (PVCAP with synergist) appears to be more effective in delaying hydrate formation as compared to PVCAP (without synergist).

- In the presence of HI03-24 inhibitor, it was observed that different degrees of subcooling (11.4 – 14.4°C) lead to different mechanisms of hydrate formation and morphologies and also hydrate appears to grow in water phase at test conditions.

- Different hydrate morphologies was observed in the presence of different kinetic inhibitors (all PVCAP-based with different synergists). This suggests that the synergist chemicals have effect on hydrate morphology and particle size for natural gas - water system.
Summary of results

- It appears that hydrate crystal growth in the presence of synergist (for HI03-22 and HI03-24) is faster than PVCAP (without synergist).
- The synergist chemicals have effect on hydrate morphology and particle size for different hydrate structure (sI and sII).
- Significant different in hydrate morphology was observed between HT03-187 and Luvicap.
Thank you