Visualization of CH4 Hydrate Dissociation Under Permafrost Temperature Conditions Using High-Pressure Micromodel

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Visualization of CH$_4$ Hydrate Dissociation Under Permafrost Temperature Conditions Using High-Pressure Micromodel*

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Gas Hydrate Studies using High Pressure Micromodels

Methane hydrate dissociation below subzero

Oral Presentation in GRS

CH$_4$/CO$_2$ Mixed Hydrate, Formation & Dissociation Behavior

Poster Presentation in GRC

CO$_2$ Injection into Methane Hydrate

Low Saturation
High Saturation
Liquid CO2
Gaseous CO2
Supporting Studies


Methodology

- Hydrate formation above 0°C
- Cooling down to near 0°C or below 0°C
- Dissociation by pressure reduction
- Dissociation at constant pressure
- Dissociation by thermal stimulation

- To observe the ice formation / change in the hydrate texture
- To observe the dissociation behavior below 0°C and/or in the presence of ice/supercooled water
- To observe the dissociation behavior below the stability pressure in the presence of ice/supercooled water
Setup Diagram

Mixed Hydrate, CO₂ Pump is attached
Labotatory setup

- Silicon wafer etched thin section (DRIE)
- Pore network of Berea Sandstone
- Water wet
- Constant vertical depth = 25 µm
- Porosity=0.61
- Pore diameter = 100 µm
- High Pressure= 100 bar
- Borosilicate glass, anionic bonding, oxide layer
- Aluminum manifold with nanoport

Capillary pressures were insignificant as pore sizes > 1 µm

Water wet, so pore filling (PF) hydrates observed
Pore Filling

Hydrate

Liberated

Gas Phase

Water in pore space

Free gas

Pore Space

Water wet grains

Saturation Increases Relative Permeability of gas decreases

Residual water saturation due to water wet grains
Hydrate Formation
Pressure = 80 bar
Temp = 0.8°C

Decrease in permeability
Formation Mechanism

Initial Gas/Water

Gas Solubility in Water

Hydrate Crystal formed

Distribution 1

- Overall three distributions
  - Hydrate Film
  - Hydrate Crystals
  - Hydrate Film & crystals

Observation

Hydrate Film formed

Hydrate Film & Crystal formed

Distribution 2

Distribution 3

- Grain
- Gas
- Hydrate Film (HF)
- Grain with GC (Hydrate Crystals)
Observation
- Hydrate can be formed
  - Methane saturated water crystallize
  - Gas pockets surrounded by water

Take away & Known information
- Hydrate formed at gas-water interface are more porous in nature
- Hydrate film color is based on layer of gas around it, Higher the gas thickness above, darker is the hydrate shells
- Thickness of hydrate around gas is controlled by mass transfer/insufficient gas pressure
- Porous /non porous hydrate could be inferred from image analysis
- Isolated gas bubbles in small pores space converted into non porous hydrate
- Excess gas, hydrate film, if excess water, hydrate crystals.
- Initial water & gas availability control the hydrate redistribution & hydrate saturation
- Hydrate rearrangement is independent of driving force
# Experimental Plan

<table>
<thead>
<tr>
<th>run</th>
<th>T(°C)</th>
<th>Siw</th>
<th>Sig</th>
<th>SW</th>
<th>Sg</th>
<th>S_H</th>
<th>Hydrate Saturation</th>
<th>Morphology observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>run#1</td>
<td>0.9</td>
<td>10%</td>
<td>90%</td>
<td>1%</td>
<td>6%</td>
<td>93%</td>
<td>High</td>
<td>HF, FG, FW</td>
</tr>
<tr>
<td>run#2</td>
<td>0.8</td>
<td>93%</td>
<td>7%</td>
<td>92%</td>
<td>0%</td>
<td>8%</td>
<td>Low</td>
<td>HC, FW</td>
</tr>
<tr>
<td>run#3</td>
<td>1.0</td>
<td>61%</td>
<td>39%</td>
<td>3%</td>
<td>8%</td>
<td>88%</td>
<td>High</td>
<td>HF, HC, FG</td>
</tr>
<tr>
<td>run#4</td>
<td>1.4</td>
<td>57%</td>
<td>44%</td>
<td>1%</td>
<td>5%</td>
<td>95%</td>
<td>High</td>
<td>HF+FG+FW</td>
</tr>
<tr>
<td>run#5</td>
<td>1.5</td>
<td>56%</td>
<td>44%</td>
<td>16%</td>
<td>0%</td>
<td>84%</td>
<td>High</td>
<td>HC+FW</td>
</tr>
<tr>
<td>run#6</td>
<td>1.7</td>
<td>50%</td>
<td>50%</td>
<td>7%</td>
<td>2%</td>
<td>91%</td>
<td>High</td>
<td>HF+HC+FW+FG</td>
</tr>
<tr>
<td>run#7</td>
<td>1.9</td>
<td>53%</td>
<td>47%</td>
<td>12%</td>
<td>1%</td>
<td>87%</td>
<td>High</td>
<td>HF+FW+FG</td>
</tr>
<tr>
<td>run#8</td>
<td>2.0</td>
<td>87%</td>
<td>14%</td>
<td>74%</td>
<td>1%</td>
<td>25%</td>
<td>Low</td>
<td>HF+HC+FW+FG</td>
</tr>
</tbody>
</table>
Different response

Dissociation Rate

Dissociation pattern

Faster

Silicon

Gas

Silicon

Slower

Hydrate Thickness

Hydrate Melting

Gas

Dissociating neighbor hydrates

Silicon

HC

Hydrate Melting
Free gas assisted dissociation

- **Take away**
  - Free gas lead to accelerated hydrate dissociation by depressurization
    - Faster mass transport through continuous gas phase
  - Hydrate Reservoirs with high hydrate saturation and no free gas
    - Depressurization not efficient method and combination with other methods are recommended.
Dissociation rate & Mobilization of gas

- Low saturation
  - Hydrate Films
  - Hydrates with Free gas

- High saturation
  - Hydrate Crystals
  - Hydrates with water or no free gas

Efficient Production method
Hydrate Dissociation
Experiment 3
Temp = 0.8°C
Saturation
Hydrate Crystals
Hydrate Shells

$P_{\text{Initial}} = 60 \text{ bar}$
$\text{Gas } \Delta q/t = 10 \text{ mL/hour}$
<table>
<thead>
<tr>
<th>Run#</th>
<th>T(°C)</th>
<th>Sh</th>
<th>Hydrate pattern</th>
<th>ΔP</th>
<th>Δt (min)</th>
<th>Observations</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Start (P&lt;sub&gt;i&lt;/sub&gt;)</td>
<td>P&lt;sub&gt;d&lt;/sub&gt;</td>
<td>ΔP</td>
<td>P&lt;sub&gt;f&lt;/sub&gt;</td>
</tr>
<tr>
<td>run#1</td>
<td>0.9</td>
<td>93%</td>
<td>HF+FG+FW</td>
<td>85</td>
<td>34,8</td>
<td>50,2</td>
<td>14</td>
</tr>
<tr>
<td>run#2</td>
<td>0.8</td>
<td>8%</td>
<td>HC+FW</td>
<td>76</td>
<td>20,4</td>
<td>55,6</td>
<td>14</td>
</tr>
<tr>
<td>run#3</td>
<td>1.0</td>
<td>88%</td>
<td>HF+HC+FG</td>
<td>60</td>
<td>18,3</td>
<td>41,7</td>
<td>14</td>
</tr>
<tr>
<td>run#4</td>
<td>-0.5</td>
<td>93%</td>
<td>HF+FG+FW</td>
<td>79</td>
<td>23,6</td>
<td>55,4</td>
<td>20</td>
</tr>
<tr>
<td>run#5</td>
<td>-0.2</td>
<td>90%</td>
<td>HC+FW</td>
<td>71</td>
<td>71</td>
<td>1,4</td>
<td>2905</td>
</tr>
<tr>
<td>run#6</td>
<td>-2.8</td>
<td>93%</td>
<td>HF+HC+FW+F</td>
<td>80</td>
<td>18</td>
<td>62</td>
<td>5,6</td>
</tr>
<tr>
<td>run#7</td>
<td>-2.6</td>
<td>87%</td>
<td>HF+FW+FG</td>
<td>55</td>
<td>15</td>
<td>40</td>
<td>14,3</td>
</tr>
<tr>
<td>run#8</td>
<td>-2.6</td>
<td>24%</td>
<td>HF+HC+FW+F</td>
<td>80</td>
<td>13</td>
<td>67</td>
<td>5</td>
</tr>
</tbody>
</table>

**Legend:**
- **FD** indicates freezing depression.
- **Dep** indicates depression.
- **SP** indicates sample preparation.
- **RF** indicates relative fluid.
Effect of Temperature on Dissociation Rate

Take away 4
- No ice reformation during depressurization
- Hydrate Crystals, depressurization, not sufficient

Hydrate shells + free gas + water

T = -0.5°C

P = 71 bar  Δt = 33 min

P = 22.8 bar  Δt = 9 min

P = 20 bar

Exp -4

Hydrate Fully dissociated

Exp -5

Hydrate Crystals

T = -0.5°C

P = 71 bar  Δt = 85 min

P = 12 bar  Δt = 47.8 hours

P = 1.4 bar  Δt = 6.15 min

P = 1.4 bar

No Dissociation during depressurization

Temperature increase
HS+ HC+ Water + Free gas

<table>
<thead>
<tr>
<th>P</th>
<th>Δt</th>
<th>Δt</th>
<th>P</th>
<th>Δt</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 bar</td>
<td>59 min</td>
<td>47.8 hours</td>
<td>5.6 bar</td>
<td>44 min</td>
<td>5.6 bar</td>
</tr>
<tr>
<td>T=2.5°C</td>
<td>T=-2.6°C</td>
<td>T=-2.6°C</td>
<td>T=-2.6°C</td>
<td>T=0.9°C</td>
<td>Exp -6</td>
</tr>
</tbody>
</table>

Hydrate Shells + Water + Free gas

<table>
<thead>
<tr>
<th>P</th>
<th>Δt</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 bar</td>
<td>73 min</td>
</tr>
<tr>
<td>T=-2.6°C</td>
<td>T=-2.6°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P</th>
<th>Δt</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.3 bar</td>
<td>2 min</td>
</tr>
</tbody>
</table>

Exp -6
Reformation

Take away 5
- Ice reformation is observed during depressurization
- High Self preservation
- Temp stimulation took longer time due to ice melting first
Self preservation & reformation

- Hydrate film show weaker self preservation tendency (no self preservation) compare to hydrate crystals
- Reformed hydrates are in the form of hydrate films, not crystalline in nature, hence porous and less stable hydrates.
- Excess water leads to higher risk of reformation/ice formation
- Risk of reformation higher at negative temperature
- Permafrost gas deposits could either coexists with supercooled water or ice along with isolated gas pockets.
Dissociation behavior in Permafrost at high negative temperature (-2⁰C or below)

- **Permafrost Hydrate Deposits**
  - **High Saturation**
    - Hydrate film
      - Faster dissociation
    - Hydrate Crystals
      - Slower dissociation
      - Gas being trapped
  - **Low Saturation**
    - Reformation
      - Ice formation
      - Self Preservation
    - Ice saturation
      - Self Preservation

Full depressurization is not effective technique for Gas production
**Hydrate Dissociation**

- Dissociation of hydrates

**Immobile gas bubbles**

- High saturation in pore filling hydrate
- Low relative permeability of gas
- Low permeability
- Shield effect from reformation

**Coalesce together**

- Permeability
- Relative permeability of fluid phase (gas permeability)

**Mobile gas phase**

- Supported by free gas in surrounding
- Low saturation, low pore filling hydrate
- High permeability
- High relative permeability of gas

**Immobile gas bubbles**

- Reformation

- Water availability
- Low temperature
- High solubility of gas in water

**Trapped in Hydrates**

- High saturation in pore filling hydrate
- Low relative permeability of gas
- Low permeability
- Shield effect from reformation

**Pore filling hydrates**
Final Conclusion

• Micromodel based pore level study provide insights about kinetics of hydrate formation and dissociation.

• Initial information such as hydrate saturation, free gas presence is critical for selection of efficient production technique.

• Subzero temperature, make dissociation slower due to self preservation tendency shown by hydrate as well as increase risk of ice and hydrate reformation. Thus, depressurization is not efficient method for gas production in permafrost hydrate reservoirs.
Acknowledgement

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Thank you!