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

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Citation (APA):
Visualization of CH₄ 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 CO$_2$
- Gaseous CO$_2$
Supporting Studies


Methodology

- **Hydrate formation above 0°C**
  - To observe the ice formation / change in the hydrate texture

- **Cooling down to near 0°C or below 0°C**
  - To observe the dissociation behavior below 0°C and/or in the presence of ice/supercooled water

- **Dissociation by pressure reduction**

- **Dissociation at constant pressure**
  - To observe the dissociation behavior below the stability pressure in the presence of ice/supercooled water

- **Dissociation by thermal stimulation**
Setup Diagram

Mixed Hydrate, CO$_2$ Pump is attached

**Diagram Details:**
- High Pressure Silicon Micromodel
- Valve
- HP Water Pump
- Unused (closed)
- Port 1, Port 2, Port 3, Port 4
- Valve open to atmosphere
- HP Gas Pump
- Data Acquisition System
- Microscope
- Light Source
- Camera
- Water
- Coolant
- Stand
- Side View
- Cooling Bath Circulation
Laboratory 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

Saturation Increases Relative Permeability of gas decreases

Water wet grains

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

Hydrate Film formed

Hydrate Film & Crystal formed

Distribution 1

Distribution 2

Distribution 3

Observation
- Overall three distributions
  - Hydrate Film
  - Hydrate Crystals
  - Hydrate Film & 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>SH %</th>
<th>Hydrate Saturation</th>
<th>Morphology observed</th>
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</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>
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<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>
Hydrate Thickness

Different response

Dissociation Rate

Dissociation pattern

Faster

Slower

Gas

Silicon

Hydrate Melting

Dissociating neighbor hydrates

Gas

HC

Silicon

Silicon

Silicon

Silicon

Silicon

G
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.
Hydrate Films

Hydrates with Free gas

Low saturation

High saturation

Efficient Production method

Dissociation rate & Mobilization of gas

Hydrate Crystals

Hydrates with water or no free gas
Hydrate Dissociation
Experiment 3
Temp = 0.8°C
Saturation
Hydrate Crystals
Hydrate Shells

$P_{\text{Initial}} = 60 \text{ bar}$
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>
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<td></td>
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<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>
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<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></td>
</tr>
<tr>
<td>run#6</td>
<td>-2.8</td>
<td>93 %</td>
<td>HF+HC+FW+FG</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+FG</td>
<td>80</td>
<td>13</td>
<td>67</td>
<td>5</td>
</tr>
</tbody>
</table>

**ΔP**

- ΔP: Start pressure (P<sub>i</sub>) - Final pressure (P<sub>f</sub>)
- ΔP: Pressure drop
- Δt: Time difference

**Observations**

- FD: Freeze dry
- Dep: Deposition
- SP, no FD: Sublimation, no freeze dry
- RF: Refluxation
Effect of Temperature on Dissociation Rate

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

Hydrate shells + free gas + water

Δt = 85 min

P = 71 bar

T = -0.5°C

Δt = 33 min

P = 22.8 bar

T = -0.5°C

Δt = 9 min

P = 20 bar

T = -0.5°C

Hydrate crystals

Δt = 47.8 hours

P = 12 bar

Δt = 6.15 min

P = 1.4 bar

Hydrate Fully dissociated

Hydrate Crystals

Δt = 4 • No ice reformation during depressurization
• Hydrate Crystals, depressurization, not sufficient

Temperature increase
HS+ HC+ Water + Free gas

$T = \text{-2.9°C}$

$T = \text{-2.9°C}$

$T = \text{-2.9°C}$

$T = \text{-2.9°C}$

Exp -8

$P = 80 \text{ bar}$  $\Delta t = 83 \text{min}$

$P = 5 \text{ bar}$  $\Delta t = 48 \text{ mins}$

$P = 13 \text{ bar}$  $\Delta t = 55.8 \text{ hours}$

$P = 13 \text{ bar}$

$P = 5 \text{ bar}$

$\Delta t = 7 \text{ min}$

$\Delta t = 10 \text{ mins}$

$\Delta t = 28 \text{ mins}$

$T = \text{-2.7°C}$

$T = \text{0.4°C}$

$T = \text{0.8°C}$

$T = \text{1.1°C}$

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 (\(-2^\circ\text{C}\) 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
- Self Preservation due to ice/supercooled water
- Hydrate crystals, Hydrate films

Hydrate Dissociation → Immobile gas bubbles → Coalesce together → Mobile gas phase

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

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!