Methane production from CO$_2$ injection in hydrates - CO$_2$ and CH$_4$ hydrate formation at pore scale

L.P. Hauge, Jarand Gauteplass, M. Høyland, A. Graue, G. Ersland, M. Fernø

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Gas hydrate as energy source

• Vast amount of energy stored in natural gas hydrates
• Location
  – Permafrost regions
  – Deep sea continental shelves
• Production mechanisms
  – Pressure depletion
  – Thermal stimulation
  – Inhibitor injection
  – CO$_2$ injection

Motivation

• Develop a new methodology to repeatedly form \( \text{CO}_2 \) and \( \text{CH}_4 \) hydrates in high pressure 2D porous medium
• Visualize and identify pore-level hydrate growth mechanisms
• Quantify hydrate growth rates in pore structures at reservoir conditions
• Provide an improved framework for fundamental studies of sediment-hosted gas hydrates
Laboratory setup

- High pressure
  - Quizix SP-5200 pump system
- Low temperature
  - Double chamber cooling system
- Dynamic imaging
  - Nikon SMZ 1500 microscope body / Nikon D7100 camera
- Porous medium
  - HP silicon micromodel
HP Etched-silicon micromodel

- Based on Berea sandstone
- DRIE etching technique (depth 25 µm)
- Accurate and well-defined pore geometry
- High coordination number (>4)
- Net pressure 10 MPa (1450 psi)
System description

Diagram showing a pore network with flow distribution channels, ports, and a field of view. The diagram also includes a micromodel with circulating antifreeze and refrigerated bath for water and gas.
# Hydrate formation

<table>
<thead>
<tr>
<th>Guest Molecule</th>
<th>$T_{\text{Initiation}}$ [°C]</th>
<th>P [MPa]</th>
<th>Cycle</th>
<th>Induction time</th>
<th>Agitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.5</td>
<td>5.8</td>
<td>Primary</td>
<td>11 days</td>
<td>Pressure pulse</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.5</td>
<td>8.0</td>
<td>Primary</td>
<td>9 days</td>
<td>Pressure pulse</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>4.4</td>
<td>8.0</td>
<td>Secondary</td>
<td>2 hrs</td>
<td>Temp +/-</td>
</tr>
</tbody>
</table>
Hydrate growth rates

![Graph showing hydrate growth rates with data points and trend lines.]

The graph illustrates the relationship between distance and time for hydrate growth rates. The data points are categorized by different symbols and lines, indicating various growth conditions or phases. The image on the right shows a microscopic view of hydrate structures, with measurements marked at 200 µm.
Dynamic hydrate distribution

Secondary Methane Hydrate Formation P=8 MPa, T=4.4°C

Formation in gas-filled pores: Area 1/Figure 7 in article. Speed: 100%
Degree of subcooling

Secondary Methane Hydrate formation (P = 8 MPa), 100% Speed

5.1 Degree C

Hydrates start forming in gas-filled pores, on the interface between gas and a water film coating the surfaces. The newly formed hydrate surface acts as a growth site for further formation, resulting in a continuous formation through clusters of gas-filled pores. Hydrate growth is faster along the pore walls than towards the center of the pore.
Hydrate rearrangement

- Rearrangement into crystalline hydrate structure
- No hydrate formation in water-saturated pores
Conclusions

- HP silicon micromodel enables high spatial resolution imaging of CO$_2$ and CH$_4$ hydrate growth in realistic and well-defined pore structures
- Hydrate formation rate depends on local accessibility of water and gas and degree of subcooling. The average CH$_4$ hydrate growth rate (at 4.4°C):
  - Alongside the pore wall ~500 μm/s
  - Towards pore center ~7 μm/s
Conclusions

- Hydrate growth pattern is strongly coupled to the local fluid distribution and fluid connectivity within the pore network.
  - (1) A thin hydrate film growing widespread on the water/gas interfaces
  - (2) A thicker hydrate layer progressing along the pore wall and toward the pore center
  - (3) Rearrangement from agglomerated polycrystalline to crystalline hydrate structure occurring over several hours
Additional