Methane Hydrate Formation, Storage and Dissociation Behavior in Unconsolidated Sediments in the Presence of Environment-friendly Promoters

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Methane Hydrate Formation, Storage and Dissociation Behavior in Unconsolidated Sediments in the Presence of Environment-friendly Promoters

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Technical University of Denmark
Presentation Outline

• Introduction

• Objective

• Experimental setup

• Experimental results

• Conclusion
Introduction: Gas Hydrates & Applications

**What Are Gas Hydrates**
- Ice-like, crystalline structures
- Common hydrate formers: methane, ethane, propane, carbon dioxide, hydrogen sulfide, nitrogen, hydrogen

**Applications**
- Natural Gas Hydrate
  - Permafrost onshore
  - Methane Production & CO₂ Storage
- Marine Sediments
  - Methane Production & CO₂ Storage
- Gas Storage
- Gas Capture & Separation
- CO₂/CH₄ Separation
- Desalination
- CO₂ hydrate based
- Refrigeration
- CO₂ hydrate based

**Flow Assurance in Oil & gas**

**Gas Hydrate Formation**

- Methane Hydrate Formation

**Gas storage capacity in hydrates**

- 1 m³ Hydrate → ~164 m³ Gas at STP + 0.9 m³ Water

**Water cages**

- 5₁²
- 5₁²₂
- 5₁²₆

**Burning hydrate**
Introduction: Role of Chemicals in Gas Hydrates

Chemicals can influence:
- Surface tension
- Solubility
- Gas diffusion

Type of Chemicals

- Accelerate hydrate formation
  - Thermodynamic enhancement
  - Kinetic enhancement
- Delay hydrate formation
  - Thermodynamic delay
  - Kinetic Delay

Why Amino Acids?

Available Chemicals
- Toxic
- Create foam
- Expensive/Large Quantity
- Environment Friendly
- Biodegradable

Amino Acids
- No Foam
- Expensive/Large Quantity
Introduction Porous Media & Promoter

- Gas hydrate formation
- Mass transfer
- Promoters
- Concentration
- Heat transfer
- Porous medium
- Specific area
- Particle size
Objective

- To study the methane hydrate formation kinetics
  - Change in particle size
  - Presence of chemicals (Amino acids & Surfactant)
- To study the dissociation kinetics
Experimental Setup

Rocking Cell (PSL Germany)

- Rocking Rate, Rocking Angle
- Volume
- Temperature Ramping, Constant Temperature

- A- Bathtub
- B- High Pressure Cell
- C- Rocking Balls
## Experimental Setup: Method and Materials

<table>
<thead>
<tr>
<th>Sand</th>
<th>Silica Sand (4 Particle Sizes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• 46.4-245 µm</td>
</tr>
<tr>
<td></td>
<td>• 160-630 µm</td>
</tr>
<tr>
<td></td>
<td>• 480-1800 µm</td>
</tr>
<tr>
<td></td>
<td>• 1400-5000 µm</td>
</tr>
<tr>
<td>Amino acids (3000 ppm concentration)</td>
<td>• L-valine</td>
</tr>
<tr>
<td></td>
<td>• L-methionine</td>
</tr>
<tr>
<td></td>
<td>• L-histidine</td>
</tr>
<tr>
<td>Sodium dodecyl Sulfate (SDS)</td>
<td>500-3000 ppm (500,1000,2000,3000 ppm)</td>
</tr>
<tr>
<td>Experimental conditions</td>
<td>100 bar, 1°C, Isothermal experiments</td>
</tr>
<tr>
<td>Parameter calculated</td>
<td>Induction time, gas uptake &amp; dissociation rate below 0°C</td>
</tr>
</tbody>
</table>
Experimental Results- Formation Kinetics

• Hydrate morphology
  – Pore filling
  – Grain coating

• Formation kinetic (Gas-liquid contact interface)
  – Grain coating – Particle surface area
  – Pore filling - Pore space
  – Large particle size: higher pore space - Large gas-liquid contact area
  – Small particle size : weak pore connectivity, barrier to mass transfer due to high capillary forces in smaller pore space

• $S_{wi} = 35\%$ change in grain coating to pore filling
Formation-Induction time

- Pressure variation during Isothermal experiments at P=100 bar and 1°C
- for given sand particle size
- Induction time is lower for SDS / Hydrophobic amino acids for any given particle size
Formation-Induction time

- Induction time is lower for SDS / Hydrophobic amino acids for any given particle size.
- Increase in particle size lead to decrease in induction time.
- L methionine and SDS have similar induction time.
- Histidine could only formed hydrate at higher sand particle size.
- Enhanced driving force due to large gas-liquid interface
Gas Uptake

- Pressure variation during Isothermal experiments at P= 100 bar and 1°C

- For low concentration (500 ppm), increase in particle size lead to decrease in gas uptake.

- At higher concentration, effect of sand particle size reduce and role of mass transfer increase

- For large particle size, change in concentration marginally affect gas uptake.

- For smaller particle size, change in concentration had dominating effect on gas uptake
Experimental Results - Dissociation

- Dissociation under $T = 266.7 \, \text{K}$ at starting pressure $P = 1 \, \text{bar}$.
- Self preservation of hydrates, Surrounded by ice sheet
- Dissociation rate is dependent on initial hydrate saturation.
- SDS/Hydrophobic amino acids dissociate faster
- SDS dissociate fastest for given sand particle while amino acids dissociated slower due to enhance hydrogen bonding
Conclusions

• $S_{wi}$ controls formation kinetics.
• Low promoter concentration, particle size effect dominates the formation kinetics dominates.
• Hydrophobic amino acids have similar kinetic behavior as SDS. Less deviation between amino acids and SDS at large particle size.
• Methane hydrate self preservation in the presence of hydrophobic amino acids enhanced.
Relevant Papers


ACKNOWLEDGEMENTS / THANK YOU / QUESTIONS

For further discussion
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