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

Pandey, Jyoti Shanker; Daas, Yousef Jouljamal; von Solms, Nicolas

Publication date: 2020

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Paper No. SPE-200532-MS
Methane Hydrate Formation, Storage and Dissociation Behavior in Unconsolidated Sediments in the Presence of Environment-friendly Promoters

Jyoti Shanker Pandey, Yousef Jouljamal Daas, and Nicolas von Solms
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**
  - Permafrost onshore
  - Marine Sediments
  - Gas Storage
  - Gas Capture & Separation
  - Desalination
  - Refrigeration
  - Methane Production & CO₂ Storage
  - Natural Gas Storage/Transport
  - CO₂/CH₄ Separation
  - CO₂ hydrate based

Gas storage capacity in hydrates:

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

Man Made Hydrate

Flow Assurance in Oil & gas

Methane Hydrate Formation
Introduction: Role of Chemicals in Gas Hydrates

Chemicals for Gas Hydrate

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

Type of Chemicals

- Promoters
- Inhibitors

Why Amino Acids?

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

Amino Acids
- No Foam
- Expensive/Large Quantity

Chemicals can influence
- Surface tension
- Solubility
- Gas diffusion

Amino Acids?

Environment Friendly - biodegradable
No Foam
Expensive/Large Quantity
Introduction Porous Media & Promoter

Gas hydrate formation

- Mass transfer
- Heat transfer

Promoters

- Concentration
- Specific area
- Particle size

Porous medium
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>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amino acids (3000 ppm concentration)</th>
<th>L-valine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L-methionine</td>
</tr>
<tr>
<td></td>
<td>L-histidine</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sodium dodecyl Sulfate (SDS)</th>
<th>500-3000 ppm (500,1000,2000,3000 ppm)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>100 bar, 1°C, Isothermal experiments</th>
</tr>
</thead>
<tbody>
<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℃

- 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 $T = 266.7$ K at starting pressure $P = 1$ 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
jyshp@kt.dtu.dk