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

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
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
- Methane Production & CO₂ Storage
- Marine Sediments
- Methane Production & CO₂ Storage
- Gas Storage
- Natural Gas Storage/Transport
- Gas Capture & Separation
- CO₂/CH₄ Separation
- Desalination
- CO₂ hydrate based
- Refrigeration
- CO₂ hydrate based

Flow Assurance in Oil & gas

Water cages

1 m³ Hydrate
~164 m³ Gas at STP
+ 0.9 m³ Water
Introduction: Role of Chemicals in Gas Hydrates

Type of Chemicals

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

Why Amino Acids?

Amino Acids vs. Available Chemicals
- Toxic
- Create foam
- Expensive/Large Quantity
- Environment Friendly
- No Foam
- Expensive/Large Quantity

Why Amino Acids?

- Environment friendly
- Biodegradable
- No foam
- Expensive/Large quantity

Chemicals can influence:
- Surface tension
- Solubility
- Gas diffusion
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></th>
<th>Silica Sand (4 Particle Sizes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</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 $1^\circ$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 $T = 266.7$ 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

• $S_{\text{wi}}$ 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