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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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

Gas storage capacity in hydrates

Gas storage capacity: 
- 1 m³ Hydrate
- ~164 m³ Gas at STP
- 0.9 m³ Water

• Applications

Natural Gas Hydrate
- Permafrost onshore
- Marine Sediments

Man Made Hydrate
- Gas Storage
- Gas Capture & Separation
- Desalination
- Refrigeration
- Flow Assurance in Oil & gas

Methane Production & CO₂ Storage
- Natural Gas Storage/Transport
- CO₂/CH₄ Separation
- CO₂ hydrate based
- CO₂ hydrate based
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?

- Promoters
- Inhibitors

Available Chemicals
- Toxic
- Create foam
- Expensive/Large Quantity
- Environment-friendly

Amino Acids
- No Foam
- Expensive/Large Quantity

Chemicals can influence
- Surface tension
- Solubility
- Gas diffusion

Amino Acids
- Available
- 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 Rate, Rocking Angle
- Volume
- Temperature Ramping, Constant Temperature

- A- Bathtub
- B- High Pressure Cell
- C- Rocking Balls

Rocking Cell (PSL Germany)
## 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>

| Sodium dodecyl Sulfate (SDS)              | 500-3000 ppm (500,1000,2000,3000 ppm)                            |

| Experimental conditions                   | 100 bar, 1°C, Isothermal experiments                             |

| Parameter calculated                      | Induction time, gas uptake & dissociation rate below 0°C        |
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 $1^\circ$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
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