PETE 310

Lectures # 33 & # 34

Chapter 17
Gas Hydrates
Prediction & Control
Hydrates Definition

“Natural gas hydrates are *ice-like* structures composed of water and natural gas molecules. Under *favorable* conditions of high pressure and low temperature, water molecules form *cages* which *encapsulate* gas molecules inside a hydrogen-bonded solid lattice”
Why Study Gas Hydrates?

- Hydrates have potential as a future energy resource
- Energy stored in methane hydrates range from 350 to 3500 years’ supply

![Pie chart showing distribution of organic carbon in Earth reservoirs](image.png)

*Distribution of organic carbon in Earth reservoirs (excluding dispersed carbon in rocks and sediments, which equals nearly 1,000 times this total amount). Numbers in gigatons (10^9 tons) of carbon.*
Why Study Gas Hydrates?

- Hydrates currently cause blocking in some underwater natural gas pipelines.
Why Study Gas Hydrates?

- Affect strength of sediments in which they are found (care in constructing underwater structures)
- Subsidence
- Safety
Gas hydrates may cause landslides on the continental slope.
Why Study Gas Hydrates?

- Hydrates have potential as a future energy resource.
Why Study Gas Hydrates?

- Hydrates have potential as a future energy resource
- Related to climate change
- Affect strength of sediments in which they are found (care in constructing underwater structures)
- Hydrates currently cause blocking in some underwater natural gas pipelines
- Hydrates may be an alternative to pipeline transmission as a way to move natural gas from deep water to the terminals of existing offshore pipelines
World Wide Locations of Natural Methane Hydrate
Storage Capacity of Hydrates

Distribution of organic carbon on Earth

- Gas hydrates: 10000
- Fossil Fuels: 5000
- Atmosphere: 3.6
- Oceans: 983
- Land: 2790

Total: 12864
A source of clean burning fuel...?
Natural Gas Hydrate on the Sea Floor
Hydrates Occurrence in Petroleum Engineering Operations

- **Production**
  
  More common, est. $500 million just for inhibition in offshore pipelines

- **Drilling**
  
  Typically during well control situations external to BOP at seafloor

- **Drill Stem Testing operations**
  
  Typically in deeper water, but definitely possible in shallow water operations
Basics Of Gas Hydrates

- General Description
- Crystal Structure
- Thermodynamic inhibition
- Hydrate Phase Behavior And Inhibition
- Kinetic inhibition
- Prediction of the hydrate phase behavior
- Remedial Actions
Crystal Structure

Cavities, guest, host
Crystal Structure of Gas Hydrates

Gas Clathrates are crystalline compounds that occur when water forms a cage-like structure around smaller guest molecules.
Definitions

- **Host** - water molecules
- **Guest** - gas molecules
Methane Hydrate Molecular Structure

Methane Hydrate Molecular Structure

ICE

CLATHRATE (HYDRATE)
- PENTAGONAL DODECAHEDRON ($5^{12}$)
- TETRAKAIDECAHEDRON ($5^{12}6^{2}$)

OXYGEN
CARBON

HYDROGEN BOND

CH$_4$

~ 4 Å
Hydrates vs Ice

- Different dielectric constant
- Different thermal conductivity

- HYDRATE: 2.23 W/m-K
- ICE: 0.5 W/m-K hydrate
Hydrate Forming Conditions

Hydrates can form when 4 ingredients are present:

- free water
- natural gas (N\textsubscript{2}, H\textsubscript{2}S, CO\textsubscript{2}, C\textsubscript{1}, C\textsubscript{2}, C\textsubscript{3}, iC\textsubscript{4})
- reduced temperature
- increased pressure
Elements Necessary for Hydrate Formation

Hydrate

- High Press.
- Low Temp.
- Water
- Natural Gas
Hydrate Modeling

How much hydrate forms and when?
Hydrate Modeling

- Three-phase V-L-S equilibria
- Need models for fugacity coefficients (solid, liquid, gas)
- Hydrate formation curves $f(P,T,\text{composition}) \rightarrow \text{saturation boundary}$
Hydrate vs No-Hydrate

Pressure

Temperature

Hydrate forms

Hydrate does not form
Hydrate Equipment

For measurement procedures see the following web site

Typical Hydrate PT Curves

Temperature /F

Pressure /psi

Tranquitas
Aguarague
Valle Morado
San Pedrito
Madrejones
Chango Norte
Lomitas
Porcelana
Ramos
Campo Duran
Ñacatimbay
Yacarecito
La Bolsa

A
B

T_A
T_B
# Typical Gas Compositions (mol %)

<table>
<thead>
<tr>
<th>Well</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>iC₄</th>
<th>nC₄</th>
<th>iC₅</th>
<th>nC₅</th>
<th>C₆⁺</th>
<th>N₂</th>
<th>CO₂</th>
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<tr>
<td>Tranquitas</td>
<td>92.09</td>
<td>2.52</td>
<td>0.51</td>
<td>0.10</td>
<td>0.12</td>
<td>0.05</td>
<td>0.04</td>
<td>0.09</td>
<td>0.56</td>
<td>3.92</td>
</tr>
<tr>
<td>Aguarague</td>
<td>92.04</td>
<td>2.82</td>
<td>0.74</td>
<td>0.14</td>
<td>0.21</td>
<td>0.10</td>
<td>0.08</td>
<td>0.25</td>
<td>0.78</td>
<td>2.84</td>
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<tr>
<td>Valle Morado</td>
<td>88.29</td>
<td>3.05</td>
<td>0.65</td>
<td>0.24</td>
<td>0.30</td>
<td>0.14</td>
<td>0.14</td>
<td>0.28</td>
<td>3.93</td>
<td>2.98</td>
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<tr>
<td>San Pedrito</td>
<td>87.77</td>
<td>4.86</td>
<td>1.51</td>
<td>0.31</td>
<td>0.41</td>
<td>0.19</td>
<td>0.12</td>
<td>0.21</td>
<td>0.87</td>
<td>3.75</td>
</tr>
</tbody>
</table>
Light Components Effect

![Graph showing the relationship between pressure and composition for two different temperatures (T = 50 F and T = 60 F). The graph plots pressure in psi on the y-axis and composition (N2 + CO2 + C1) in mol% on the x-axis. The data points are represented with blue and orange dots for T = 50 F and T = 60 F, respectively.]
Hydrates: Remedies

Once hydrates have formed what can be done to remove them?

- reduce pressure
- increase temperature
- chemical (thermodynamic) inhibition
- kinetic inhibitors
- mechanical removal
Hydrates: Prevention

- Remove any of the 4 ingredients
- Thermodynamic inhibitors
  - electrolytes (salts) form ionic bonds with free water
  - polar compounds (alcohols, glycols) compete with hydrates for hydrogen bonding
Thermodynamic Inhibitors

- Salts
- Alcohols
- Glycols
Hydrates: Prevention

Salts

- Normally sodium chloride, 20-24% by wt.
- Potassium chloride can be used but it is significantly more expensive, and saturated KCl muds have performed poorly in offshore environments.
- Calcium Chloride, very expensive and not as effective as NaCl for hydrate suppression.
Salt Inhibitors

- Salt ionizes in solution and interacts with the dipoles of the water molecules and causes clustering.
- This clustering also causes a decrease in the solubility of potential hydrate guest molecules in the water.
- These combine to require substantially more subcooling to cause hydrates to form.

Examples: Sodium Chloride and Calcium Chloride.
Alcohol Inhibitors

- The Hydroxyl Group Hydrogen Bonds The Water Molecules. In Direct Competition With The Dissolved Apolar Molecules.

- Inhibition Ability - Decreases With Volatility

Examples:
- Methanol
- Ethanol
- Isopropanol
Glycol Inhibitors

- More Hydrogen Bonding Opportunity With Water Through One More Hydroxyl Group Than Alcohols
- Glycols Generally Have Higher Molecular Weights Which Inhibit Volatility

Examples
- Ethylene Glycol
- Triethylene Glycol
## Common Thermodynamic Hydrate Inhibitors

<table>
<thead>
<tr>
<th>Salts</th>
<th>Alcohol/diols</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Methanol</td>
</tr>
<tr>
<td>KCl</td>
<td>Ethanol</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>Glycerol</td>
</tr>
<tr>
<td>Na-Formate</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>K-Formate</td>
<td>Propylene glycol</td>
</tr>
<tr>
<td>NaBr</td>
<td>Polyalkylene glycol</td>
</tr>
<tr>
<td>CaBr(_2)</td>
<td></td>
</tr>
<tr>
<td>ZnBr(_2)</td>
<td></td>
</tr>
</tbody>
</table>
Thermodynamic Inhibitors

Summary

- Glycols
- Alcohols
- Salts

Alcohols & Glycols when dissolved in aqueous solutions form hydrogen bond with the water molecules and make it difficult for the water molecules to participate in the hydrate structure.
Effect of NaCl

T = 60 °F

(N2 + CO2 + C1) composition/mol% vs. Pressure /psi for different NaCl concentrations: 12 wt%, 10 wt%, 5 wt%, and without NaCl.
Effect of Methanol
Hydrate Inhibitors

Salts - Effectiveness

NaCl > KCl > CaCl$_2$ > NaBr > Na Formate > Ca Nitrate

More Effective
## Typical Sample Formulations

<table>
<thead>
<tr>
<th></th>
<th>Equilibrium</th>
<th>ΔT</th>
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<tbody>
<tr>
<td></td>
<td>F°</td>
<td>psi</td>
</tr>
<tr>
<td>20% NaCl + 10% Aqua-Col</td>
<td>45</td>
<td>5360</td>
</tr>
<tr>
<td>20% NaCl + 10% HF-100</td>
<td>44.9</td>
<td>5067</td>
</tr>
<tr>
<td>20% KCl</td>
<td>66.1</td>
<td>5580</td>
</tr>
<tr>
<td>10% KCl + 10% Aqua-Col</td>
<td>71.2</td>
<td>5245</td>
</tr>
<tr>
<td>10% KCl + 10% HF-100</td>
<td>70.2</td>
<td>5460</td>
</tr>
<tr>
<td>10% KCl + 10% NaCl</td>
<td>61.6</td>
<td>4936</td>
</tr>
<tr>
<td>10% KCl + 10% NaCl + 10% Aqua-Col</td>
<td>51.0</td>
<td>4825</td>
</tr>
<tr>
<td>10% Aqua-Col</td>
<td>79.2</td>
<td>5500</td>
</tr>
<tr>
<td>20% NaFormate + 10% Aqua-Col</td>
<td>50.6</td>
<td>4570</td>
</tr>
<tr>
<td>Seawater</td>
<td>80</td>
<td>5500</td>
</tr>
</tbody>
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Kinetic Inhibitors

Strategy

- An additive(s) that renders the formed hydrate into a **pumpable** slurry.

- Focused on emulsifying environmentally acceptable synthetic oils with the objective of having the synthetic oil coat the forming hydrates, preventing agglomeration.
Kinetic Inhibitors

- Delay the onset of formation
- Slow the rate of formation
- Prevent the agglomeration of hydrates (slush)
- Reduce the amount of hydrate that form
Hydrate References
(with full articles)

Kinetics of Gas Hydrate Formation and Decomposition

http://woodshole.er.usgs.gov/project-pages/hydrates/

Fig. 17–11. Permissible expansion of 0.7 specific gravity gas without hydrate formation. (Katz, *Trans.*, AIME, 160, 140. Copyright 1945 SPE-AIME.)
Initial \( P = 2200 \text{ psia} \)

Initial \( T = 150^\circ \text{F} \)

Safe (no hydrate) final \( P = 350 \text{ psia} \) and final \( T = 50^\circ \text{F} \)

Fig. 17–11. Permissible expansion of 0.7 specific gravity gas without hydrate formation. (Katz, *Trans.*, AIME, 160, 140. Copyright 1945 SPE-AIME.)
Hydrates Summary

- Lots of research issues to pursue
- Be aware of hydrates
- Be prepared to prevent hydrate problems

- materials
- procedures
- contingencies
- site/job investigation
Remove one of the components needed for hydrates to form.
Phase Boundaries
Fig. 17–4. Hydrate-formation conditions of methane-propane mixtures.
Fig. 17–6. Hydrate-forming conditions for natural gases. (Katz, *Trans.*, AIME, 160, 140. copyright 1945 SPE-AIME.)
Fig. 17–7. Depression of hydrate-formation temperatures by inhibitors. (From Handbook of Natural Gas Engineering by Katz et al. Copyright
Serious Effects of Gas Hydrates in Drilling Operations

- Plugging of choke and kill lines
- Formation of a plug at or below BOP, preventing monitoring of pressures below BOP
- Plugging tubing, downhole tools and wireline during DST operation
- Free water tied up with hydrates can cause thickening of the mud
Remedial Actions
(Hydrate melting schemes)

- Mechanical
- Depressurization
- Chemical
- Thermal

![Graph showing hydrate stability under different conditions of pressure and temperature with and without inhibitors.](image-url)
Inhibition of Hydrates

Figure 2: Hydrate dissociation conditions a gas condensate in the presence of distilled water and methanol solutions.
Pressure, Temperature Profiles – Sea Water
Inhibition/ Dissociation of Hydrates

- Remove One Component i.e. Water, Gas
- Increase Temperature
- Decrease System Pressure
- Use an Inhibitor in the Water Phase (Thermodynamic)
Hydrate Forming Gases

- For a given $T$
  - Hydrate formation
  - $P$ increases as HC size decreases