Hydrate-Bearing Clayey Sediments: Morphology, Physical Properties, Production and Engineering/Geological Implications

Project Period (10/1/2012 to 9/30/2016)

Submitted by:
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ACCOMPLISHMENTS

**Context – Goals.** Fine grained sediments host more than 90% of the global gas hydrate accumulations. Yet, hydrate formation in clayey sediments is least understood and characterized. This research focuses on hydrate bearing clayey sediments. The goals of this research are (1) to gain a fundamental understanding of hydrate formation and ensuing morphology, (2) to develop laboratory techniques to emulate “natural” formations, (3) to assess and develop analytical tools to predict physical properties, (4) to evaluate engineering and geological implications, and (5) to advance gas production alternatives to recover methane from these sediments.

**Accomplished**
The main accomplishments for this period include:

- X-ray CT system calibration
  - Attainable image resolution
  - Design of specimen centering positioner for rotary stage
- Design and Fabrication of new high pressure chamber
  - Light, thin-walled design for X-ray CT scanning
- Analysis of effective thermal conductivity
  - Numerical solutions
- In-Lab CO₂ hydrate formation in diatoms
- In-Lab THF hydrate formation in various sediments
  - Hydrate formation in diatoms, kaolinite, and silica flour

**Plan - Next reporting period**
Research in Progress

X-ray CT Calibration
An attachment was designed and fabricated for the motorized rotary stage to attain higher accuracy in centering and positioning specimens. The result is higher quality reconstructed images due to reduced motion blurring and off-center reconstruction artifacts.

Figure 1. Motorized rotary stage with centering device.

Additionally, the system was tested to determine the minimal particle size capable of being detected at varying chamber sizes and geometric magnification distances.
**Chamber Design**

A thin-walled (3.5 mm) aluminum chamber (Ø 40mm, H 140mm) was designed and fabricated to sustain pressures up to 20 MPa. The end caps are made of steel with a total of 6 NPT ports for fluid and electronics feed through.

![Figure 2. Thin-walled aluminum high pressure chamber and steel end caps](image)

**Effective Thermal Conductivity**

A series of numerical models were implemented to narrow the range of effective thermal conductivities of hydrate-bearing fine-grained sediments with segregated hydrate morphology. The thermal properties of the segregated components were used for input into the numerical models (Table 1).
Table 1. Thermal Properties of relative components in a Hydrate-Bearing Sediment system

<table>
<thead>
<tr>
<th>Component</th>
<th>λ [W m⁻¹ K⁻¹]</th>
<th>κ [x10⁻⁷ m² s⁻¹]</th>
<th>c_p [J kg⁻¹ K⁻¹]</th>
<th>ρ [kg m⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.024ᵈ</td>
<td>183ᵈ</td>
<td>1010ᵈ</td>
<td>1.3ᵈ</td>
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<tr>
<td>Water</td>
<td>0.56ᵈ</td>
<td>1.33ᵈ</td>
<td>4220ᵈ</td>
<td>999.9ᵈ</td>
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<tr>
<td>Ice</td>
<td>2.18ᵈ</td>
<td>11.7ᵈ</td>
<td>2052ᵈ</td>
<td>917ᵈ</td>
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<tr>
<td>THF·17H₂O</td>
<td>0.47ᵃ</td>
<td>3.12</td>
<td>4080</td>
<td>982</td>
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<tr>
<td>THF·17H₂O hydrate</td>
<td>0.51ᵉ</td>
<td>2.55ᵉ</td>
<td>2020ᵉ</td>
<td>971ᵉ</td>
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<tr>
<td>CH₄·6H₂O hydrate</td>
<td>0.575ᵉ</td>
<td>3.35ˡ</td>
<td>2031ˡ</td>
<td>979ˡ</td>
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<tr>
<td>Dry clay</td>
<td>0.17ᵃ</td>
<td>1.59</td>
<td>1700</td>
<td>1600</td>
</tr>
<tr>
<td>Saturated marine clay</td>
<td>1.12ᵇ</td>
<td>3.36ᵇ</td>
<td>1960ᵇ</td>
<td>1760ᵇ</td>
</tr>
</tbody>
</table>


The validity of numerical results were compared against known analytical solution for simple cases. The model involved 3 thick layers of saturated marine clay and 2 thin hydrate layers in series.

\[
\begin{align*}
    k_{\text{eff},z} &= L_T \left( k_{\text{hyd}} \cdot k_{\text{clay}} \right) \\
    &= \frac{k_{\text{hyd}} \cdot k_{\text{clay}}}{2L_{\text{hyd}} \cdot k_{\text{clay}} + 3L_{\text{clay}} \cdot k_{\text{hyd}}}
\end{align*}
\]

<table>
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<tr>
<th>Solution Method</th>
<th>k_{\text{eff},z} [W m⁻¹ K⁻¹]</th>
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<tr>
<td>COMSOL</td>
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<tr>
<td>Analytical</td>
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</table>

Figure 3. Verification Model – Saturated marine clay + THF hydrate in series

The following study involved real hydrate structures extracted from X-ray images (a laboratory formed THF hydrate in kaolinite obtained in our lab, and in-situ natural gas hydrate in a fine-grained marine sediment from the Krishna-Godavari Basin - Priest et al. 2008).
Figure 4. Image Model - Laboratory formed THF hydrate + Kaolinite mixture

Figure 5. Image Model – In-situ natural gas hydrate + marine sediment
The thermal properties used in this case are of CH₄ hydrate and saturated marine clay from Table 1:

- Volume fraction of hydrate in medium – 36.76%
- Effective thermal conductivity in the vertical direction when medium is subjected to a 50K vertical thermal gradient – 0.806 W m⁻¹ K⁻¹
- Effective thermal conductivity in the horizontal direction when medium is subjected to a 50K horizontal thermal gradient – 0.869 W m⁻¹ K⁻¹
- Volume fraction of hydrate – 43.55%
- Effective thermal gradient in vertical direction – 0.830 W m⁻¹ K⁻¹
- Effective thermal gradient in horizontal direction – 0.780 W m⁻¹ K⁻¹

This preliminary study provides great insight into the variability of the effective properties due to the topology of hydrate lenses.

**CO₂ Hydrate Formation**

Tests were conducted to form CO₂ hydrate in diatomaceous earth. Water was injected into the system outside of hydrate stability field in test 1 (Figures 6 and 7) and inside the stability field in test 2 (Figures 8, 9 and 10). In both tests, oven dried specimen with built-in thermocouples were placed into a high pressure chamber. Several vacuum-CO₂ flooding cycles were conducted to increase CO₂ saturation and remove all N₂. Droplets of water were gradually added to the specimen.
Figure 6. Temperature-Pressure path for test 1

Figure 7. Pictures taken during the wetting process inside the stability field (the first row corresponds to the ‘Water Injection’, the second row ‘Hydrate Formation’, and the third ‘Depressurization’)

In Sample

Phase Boundary

Vacuum Iteration

Pressurization

Water Injection

Depressurization

Temperature depression

Pressure [MPa]

Temperature [°C]
Figure 8. Temperature-Pressure path for test 2

Figure 9. CO₂ Hydrate formation with water droplet added to the specimen (This corresponds to “Water Injection and Hydrate Formation” in the P-T path)
Figure 10. Growth (notice the crystal on the edge of the container) and dissociation of CO₂ hydrate (Images captured from low resolution video)

Observations:

- Cracks formed during water injection contract and vanish during hydrate formation.
- Hydrate continues growing even after PT equilibrium. Slow ice crystal formation on edges and cracks draws water from the sediment.
- Dissociation causes massive sediment disruption in this unconfined test. Yet, some of the initial sediment structure is preserved after dissociation, which indicates segregated hydrate formation.
**THF Hydrate Formation in Clay**

THF hydrate was formed in three distinct fine-grained geomaterials: diatoms, kaolinite, and silica flour. The samples were formed by first creating a THF-H₂O solution above stoichiometric ratio 1THF:13H₂O to ensure that no ice forms in the system. After thoroughly mixing the selected geomaterials with the fluid at a liquid content similar to that of each of the materials’ liquid limits, the specimens were placed in the aluminum chamber. Two thermocouples were positioned in the specimens, one directly in the center and the other ~0.5 cm below the surface and ~0.2 cm from the aluminum wall, shown in figure 11. Each of the specimens was then CT-imaged to assess the initial sediment structure and the presence of air voids. Then, specimen where subjected to temperature controlled conditions to bring the mixture inside the stability field. Thermal spikes showed hydrate formation (Figure 12). Finally, specimens were scanned again to visualize the topology of the hydrate.

![Figure 11. Schematic of thermocouples in X-ray invisible high pressure chamber](image)
Slices of the 3D tomographic image gathered after hydrate formation are shown next. In general, thicker but fewer lenses formed in diatoms, while thinner and more lenses formed in kaolinite. A structure of fine lenses occurred on the outer diameter of the kaolinite specimen. No lenses were detected in the silica flour, though hydrate did noticeably form coating air voids created during sample preparation. These results are in agreement with previous observations made by this group on the topology of hydrate formation in sediments.
Diatom + THF Hydrate
Kaolinite + THF Hydrate
Silica Flour + THF Hydrate
MILESTONE LOG

<table>
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<th>Milestone</th>
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<th>Actual completion date</th>
<th>Verification method</th>
<th>Comments</th>
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<td>5/2013</td>
<td>Report</td>
<td>Completed first phase. Will continue throughout the project</td>
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PRODUCTS

- **Publications:**
- **Presentations:**
- **Website:** Publications and key presentations are included in [http://pmrl.ce.gatech.edu/](http://pmrl.ce.gatech.edu/) (for academic purposes only)
- **Technologies or techniques:** X-ray tomographer and pressure vessel
- **Inventions, patent applications, and/or licenses:** None at this point.
- **Other products:** None at this point.
PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS

Research Team: The current team is shown next. We anticipate including external collaborators as the project advances.

[Diagram showing the research team and collaborators]

IMPACT

While it is still too early to assess impact, we can already highlight preliminary success of exploring hydrate lenses morphology in real systems, and analogue studies using a high resolution tomographer.

CHANGES/PROBLEMS:

None at this point.

SPECIAL REPORTING REQUIREMENTS:

We are progressing towards all goals for this project.

BUDGETARY INFORMATION:

As of the end of this research period, expenditures are summarized in the following table.

Note: in our academic cycle, higher expenditures typically take place during the summer quarter.
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