NATIONAL ENERGY TECHNOLOGY LABORATORY
OIL & GAS

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Quarterly Research Performance Progress Report (Period Ending 3/31/2019)

A multi-scale experimental investigation of flow properties in coarse-grained hydrate reservoirs during production

Project Period (10/1/2016-9/30/2019)

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U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Office of Fossil Energy

DISCLAIMER

1. ACCOMPLISHMENTS:

What was done? What was learned?

This report outlines the progress of the second quarter of the third fiscal year in the second budget period. Highlights from the period include:

- Our manuscript on depressurization experiments in sand packs has been accepted pending revisions. We highlight (1) the ability to estimate the sample salinity by monitoring the initial pressure of hydrate dissociation, (2) the deviation of observed pressure during dissociation from the pressure predicted by homogenous conditions, and (3) the influence of salt diffusion on the form of pressure rebounds while the sample is shut in during dissociation. These core-scale experiments may inform field scale depressurization (production).

- We used Raman mapping to understand how grain size influences hydrate distribution in interbedded coarse- and fine-grained layers (Fig. 9.1). During hydrate crystallization, comparable amounts of hydrates form in the fine-grained and coarse-grained layers (Fig. 9.2.a). In later stages, hydrates concentration in the fine layer decreases and concentration in the coarse layer increases. This behavior can be, at least partly, explained by the higher concentration of dissolved methane in the finer grained facies due to its smaller pore size and higher capillary pressure.

- We have begun to develop a systematic approach to explore 3-phase permeability (hydrate, vapor, and water). Our initial results suggest that hydrate is behaving as a non-wetting phase (like vapor) and that we can use a simple Brooks-Corey type fit to describe relative permeability.

A. What are the major goals of the project?

The goals of this project are to provide a systematic understanding of permeability, relative permeability and dissipation behavior in coarse-grained methane hydrate - sediment reservoirs. The results will inform reservoir simulation efforts, which will be critical to determining the viability of the coarse-grained hydrate reservoir as an energy resource. We will perform our investigation at the macro- (core) and micro- (pore) scale.

At the macro- (core) scale, we will: 1) measure the relative permeability of the hydrate reservoir to gas and water flow in the presence of hydrate at various pore saturations; and 2) depressurize the hydrate reservoir at a range of initial saturations to observe mass transport and at what time scale local equilibrium describes disassociation behavior. Simultaneously, at the micro (pore) scale, we will 1) use micro-CT to observe the habit of the hydrate, gas, and water phases within the pore space at a range of initial saturations and then image the evolution of these habits during dissociation, and 2) use optical micro-Raman Spectroscopy to images phases and molecules/salinity present both at initial saturations and at stages of dissociation. We will use our micro-scale observations to inform our macro-scale observations of relative permeability and dissipation behavior.

In Phase 1, we first demonstrated our ability to systematically manufacture sand-pack hydrate samples at a range of hydrate saturations. We then measured the permeability of the hydrate-saturated sand pack to flow a single brine phase and depressurized the hydrate-saturated sand packs and observed the kinetic (time-dependent) behavior. Simultaneously we built a micro-CT pressure container and a micro-Raman Spectroscopy chamber and imaged the pore-scale habit, phases, and pore fluid chemistry of sand-pack hydrate samples. We then made observations on our hydrate-saturated sand-packs.

In Phase 2, we will measure relative permeability to water and gas in the presence of hydrate in sand-packs using co-injection of water and gas. We will also extend our measurements from sand-pack models of hydrate to observations of actual Gulf of Mexico material. We will also measure relative permeability in intact samples to be recovered from the upcoming Gulf of Mexico 2017 hydrate coring expedition. We will also perform dissipation experiments on intact Gulf of Mexico pressure cores. At the micro-scale we will perform micro-Raman and micro-Ct imaging on hydrate samples composed from Gulf of Mexico sediment.

The Project Milestones are listed in the table below.

Milestone Description	Planned Completion	Actual Completion	Verification Method	Comments
Milestone 1.A: Project Kick-off Meeting	11/22/2016 (Y1Q1)	11/22/16	Presentation	Complete
Milestone 1.B: Achieve hydrate formation in sand-pack	6/27/2017 (Y1Q3)	8/11/17	Documentation of milestone achievement within required project reporting / deliverables (Deliverable 2.1)	Complete, *Documentation in the Y1Q3 quarterly and Phase 1 report*
Milestone 1.C: Controlled and measured hydrate saturation using different methods	3/27/2018 (Y2Q2)	3/27/18	Documentation of milestone achievement within required project reporting / deliverables (Deliverable 2.1)	Complete, *Documentation in Y2Q2 quarterly and Phase 1 report*
3 Milestone 1.D: Achieved depressurization and demonstrated mass balance	3/27/2018 (Y2Q2)	12/18/2017	Documentation of milestone achievement within required project reporting / deliverables (Deliverable 3.1)	Complete, *Documentation in the Y2Q1 quarterly and Phase 1 report*
Milestone 1.E: Built and tested micro-consolidation device	6/27/2017 (Y1Q3)	6/27/2017	Documentation of milestone achievement within required project reporting / deliverables (Deliverable 4.1)	Complete, *Documentation in Y1Q3 quarterly and Phase 1 report*
Milestone 1.F: Achieved Hydrate formation and measurements in Micro-CT consolidation device	3/27/2018 (Y2Q2)	2/15/18	Documentation of milestone achievement within required project reporting / deliverables (Deliverable 4.1)	Complete, *Documentation in Y2Q2 quarterly and Phase 1 report*
Milestone 1.G: Built and integrated high-pressure gas mixing chamber	3/27/2018 (Y2Q2)	6/27/17	Documentation of milestone achievement within required project reporting / deliverables (Deliverable 5.1)	Complete, *Documentation in Y1Q3 quarterly and Phase 1 report*
Milestone 1.H: Micro-Raman analysis of synthetic complex methane hydrate	3/28/2018 (Y2Q2)	3/27/18	Documentation of milestone achievement within required project reporting / deliverables (Deliverable 5.1)	Complete, *Documentation in Y2Q2 quarterly and Phase 1 report*

Milestone 2.A - Measurement of relative permeability in sand-pack cores. (See Subtask 6.1)	1/17/2019 (Y3Q2)	expected 9/30/2019	Documentation of milestone achievement within required project reporting / deliverables (Deliverable 6.1)	In progress,– we proposed to spend more time refining the experimental process.
Milestone 2.B - Measurement of relative permeability in intact pressure cores. (See Subtask 6.2)	9/30/2019 (Y3Q4)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 6.1)	
Milestone 2.C -Depressurization of intact hydrate samples and documentation of thermodynamic behavior. (See Subtask 7.1 and 7.2)	9/30/2019 (Y3Q4)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 7.1)	In progress
Milestone 2.D - Achieved gas production from GOM^2 samples monitored by micro-CT. (See Subtask 8.1 and 8.2)	9/30/2019 (Y3Q4)		Documentation of milestone achievement within required project reporting / deliverables Report (Deliverable 8.1)	In progress
Milestone 2.E - Building a chamber to prepare natural samples for 2D-3D micro-Raman analysis; (See Subtask 9.1 and 9.2)	1/17/2019 (Y3Q2)	3/31/19	Documentation of milestone achievement within required project reporting / deliverables (Deliverable 9.1)	Complete, Documentation in this report and to be included in the Phase 2 report.
Milestone 2.F - 2D micro-Raman analysis of natural methane hydrate samples at depressurization; (See Subtask 9.1 and 9.2)	9/30/2019 (Y3Q4)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 9.1)	In progress

B. What was accomplished under these goals?

PAST- BUDGET PERIOD 1

Task 1.0 Project Management and Planning

Planned Finish: 09/30/19
Actual Finish: In progress continued in Phase 2, see Task 1 below.

Task 2.0 Macro-Scale: Relative Permeability of Methane Hydrate Sand Packs

Subtask 2.1 Laboratory Creation of Sand-Pack Samples at Varying Hydrate Levels
Planned Finish: 6/ 27/17
Actual Finish: 8/11/17 Complete

Documentation of subtask completion in Y1Q4 Quarterly and the Phase 1 report per the SOPO (Deliverable 2.1).

Subtask 2.2 Steady-State Permeability of Gas and Water of Sand-Pack Hydrate Samples
Planned Finish: 3/27/18
Actual Finish: Complete

Documentation of subtask completion in Y2Q2 Quarterly and the Phase 1 report per the SOPO (Deliverable 2.1).

Task 3.0 Macro-Scale: Depressurization of Methane Hydrate Sand Packs

Subtask 3.1 Depressurization Tests
Planned Finish: 6/27/17
Actual Finish: 3/27/2018 Complete

Documentation of subtask completion in was made in the Phase 1 report per the SOPO (Deliverable 3.1).

Subtask 3.2 Depressurization Tests with CAT scan
Planned Finish: 03/27/18
Actual Finish: 3/27/2018 Complete

Documentation of subtask completion in was made in the Phase 1 report per the SOPO (Deliverable 3.1).

Task 4.0 Micro-Scale: CT Observation of Methane Hydrate Sand Packs

Subtask 4.1 Design and Build a Micro-CT compatible Pressure Vessel
Planned Finish: 6/27/17
Actual Finish: 6/27/2017 Complete

Subtask 4.2 Micro-Scale CT Observations and Analysis
Planned Finish: 03/27/18
Actual Finish: 2/15/2018 Complete

Documentation of Milestone 1.F was included in the Y2 Q2 report and the Phase 1 report per the SOPO (Deliverable 4.1)

Task 5.0 Micro-Scale: Raman Observation of Methane-Gas-Water Systems

Subtask 5.1 Design and Build a Micro-Raman compatible Pressure Vessel
Planned Finish: 6/27/17
Actual Finish: 6/27/17 Complete

Documentation of subtask completion in Y1Q3 Quarterly, Documentation of Milestone 1.G included in the Phase 1 report per the SOPO (Deliverable 5.1)

Subtask 5.2 Micro-scale petrochemistry
Planned Finish: 03/31/18
Actual Finish: 03/27/2018 Complete

Documentation of Milestone 1.H included in the Y2Q2 and Phase 1 report per the SOPO (Deliverable 5.1)

Subtask 5.3 Diffusion kinetics of methane release
Planned Finish: 3/27/18
Actual Finish: 3/27/2018

Documentation of Milestone 1.H included in the Y2Q2 and Phase 1 report per the SOPO (Deliverable 5.1)

Decision Point: Budget Period 2 Continuation

Continuation Application submitted on March 5. Continuation approved March 26, 2018.

CURRENT – BUDGET PERIOD 2

Task 1.0 Project Management and Planning

Planned Finish: 09/30/19
Actual Finish: In progress

This task continues from Phase 1.
The ninth Quarter Report was submitted on Jan 30, 2019.

Link to actions for next Quarter, Task 1

Task 6.0 Macro-Scale: Relative Permeability of Methane Hydrate Sand Packs and Intact Pressure Core Samples

Subtask 6.1 Steady-State Relative Permeability Measurements of Sand-Pack Hydrate Samples
Planned Finish: 1/17/19
Actual Finish: In Progress, expected 9/30/2019 – we have proposed to spend more time refining the experimental process.

Relative Permeability
To better control and understand the hydrate saturation and distribution in our samples, we have taken multiple CT images of our core to measure the initial water saturation and distribution. Hydrate will likely form where water is initially in the core. If the water is well distributed, the hydrate saturation will be more homogenous. We have tested multiple methods to saturate our core.

Layered Sands
The sleeves and sands for the layered sands experiment have been delivered. We have packed the vessel with 250 micrometer sand using the slow pluvation method.

Data Analysis
In addition to experimental improvements, we have been working to better understand our previously collected data. Our first question is to better understand water permeability in the presence of hydrates. Countless models have been proposed to determine krw as a function of hydrate saturation. However, none of the data seems to suggest a given model. The pore-filling and pore-coating models presented in Kleinberg et al. (2003) are frequently used in the literature. We have plotted our experimental data as well as data from other synthetic and natural samples along with the Kleinberg models in Fig. 6.1. The wide distribution shows that there is no consensus on how hydrate saturation impacts water effective permeability.

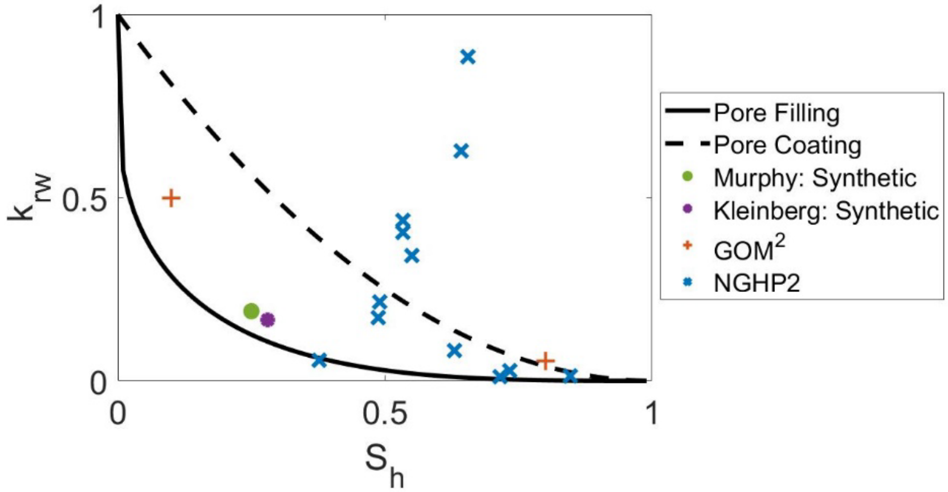

Figure 6.1. Water phase relative permeability as a function of hydrate saturation with pore-filling and pore-coating hydrate models of Kleinberg et al. (2003) for comparison.

Water relative permeability in the presence of hydrates can be measured at various hydrate saturations (as shown above). The hydrate should act as the nonwetting phase and occupies the larger pores. Therefore, the water relative permeability should be like the two-phase relative permeability for gas and water (Fig. 6.2). We have measured this relative permeability curve for our sample multiple times for nitrogen and water and fit a Brooks-Corey fit to this data.

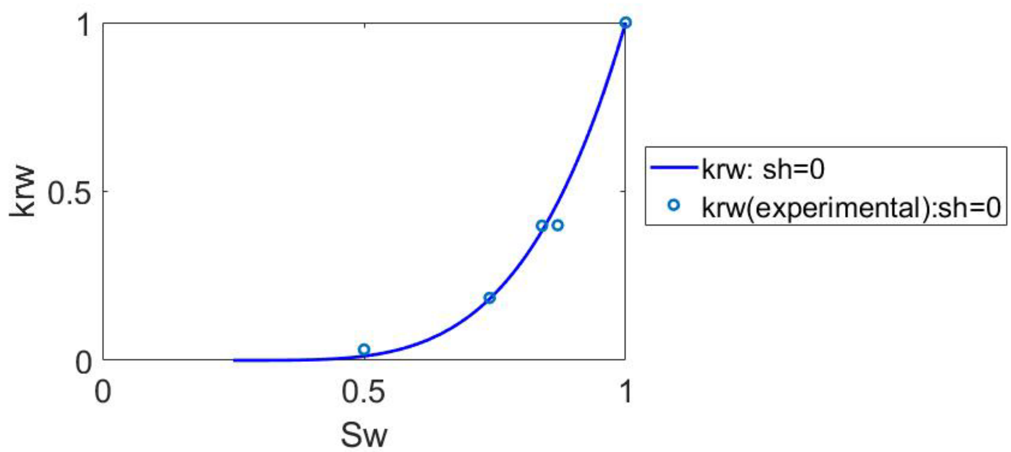

Figure 6.2. Water phase relative permeability in the presence of nitrogen for a hydrate-free Berea Sandstone sample.

If hydrate is added to the system, the hydrate should occupy the same pores as gas at a given water saturation. Therefore, the water relative permeability begins at $1\text{-}S_h$ and will follow the same functional form as the hydrate-free sample (Fig. 6.3).

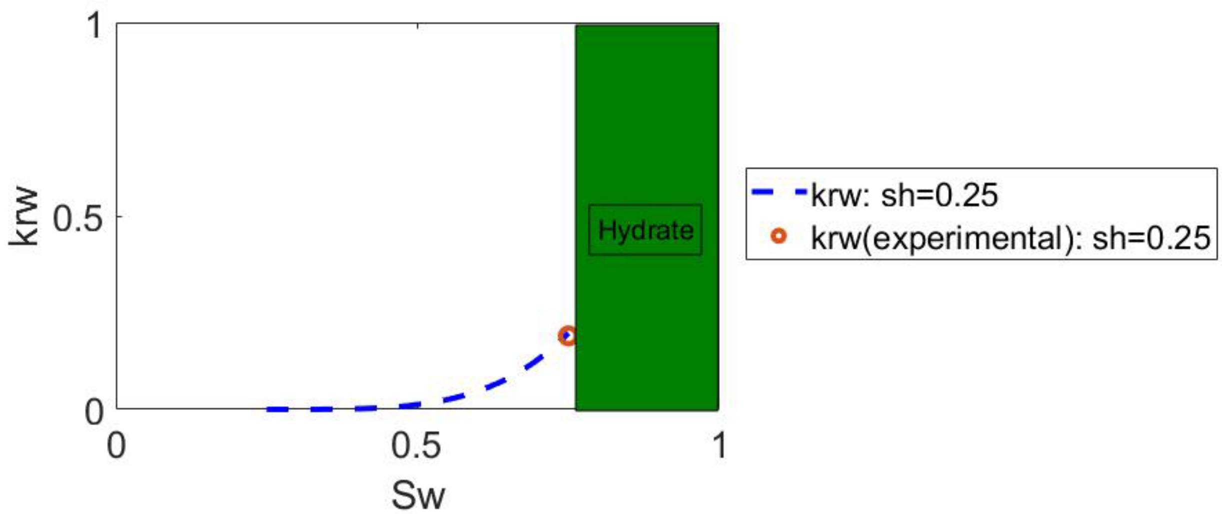

Figure 6.3. Water phase relative permeability for a Berea Sandstone where hydrate occupies 25% of the pore space. The dashed line is the same Brooks-Corey model from Figure 6.2.

We have collected the one data point that validates this curve for a Berea Sandstone but need to collect more data points at various hydrate saturations. If more data points support our initial observations, we will be able to determine the water relative permeability for a hydrate system using a simple Brooks-Corey type fit for any porous media.

Link to actions for next Quarter, Task 6

Subtask 6.2 Steady-State Relative Permeability Measurements of Intact Pressure Cores
Planned Finish: 9/30/19
Actual Finish: Not Started

Task 7.0 Macro-Scale: Depressurization of Methane Hydrate Sand Packs and Intact Pressure Core Samples

Subtask 7.1 Depressurization of sand-pack hydrate samples
Planned Finish: 1/17/19
Actual Finish: In Progress

Our manuscript on depressurization experiments in sand packs has been accepted pending revisions These results highlight (1) the ability to estimate the sample salinity by monitoring the initial pressure of hydrate dissociation, (2) the deviation of observed pressure during dissociation from the pressure predicted by homogenous conditions, and (3) influence of salt diffusion on the form of pressure rebounds while the sample is shut in during dissociation. These results show that when hydrate dissociation begins, localized freshening and cooling around the hydrate sets up salinity and temperature gradients that change the conditions around the dissociating hydrate.

Through this revision process we are beginning to better understand the role of pressure and temperature on influencing pressure rebound behavior. Over the course of dissociation, the pressure rebound curves evolve to be more concave-up in shape when plotted vs. time on a log scale, with this effect more pronounced in brine experiments than in fresh water experiments (Fig. 7.1). Salt and heat diffusion modeling show that this concave-up behavior is consistent with the combined effects of salt and heat diffusion during shut-in periods (Fig. 7.2), which

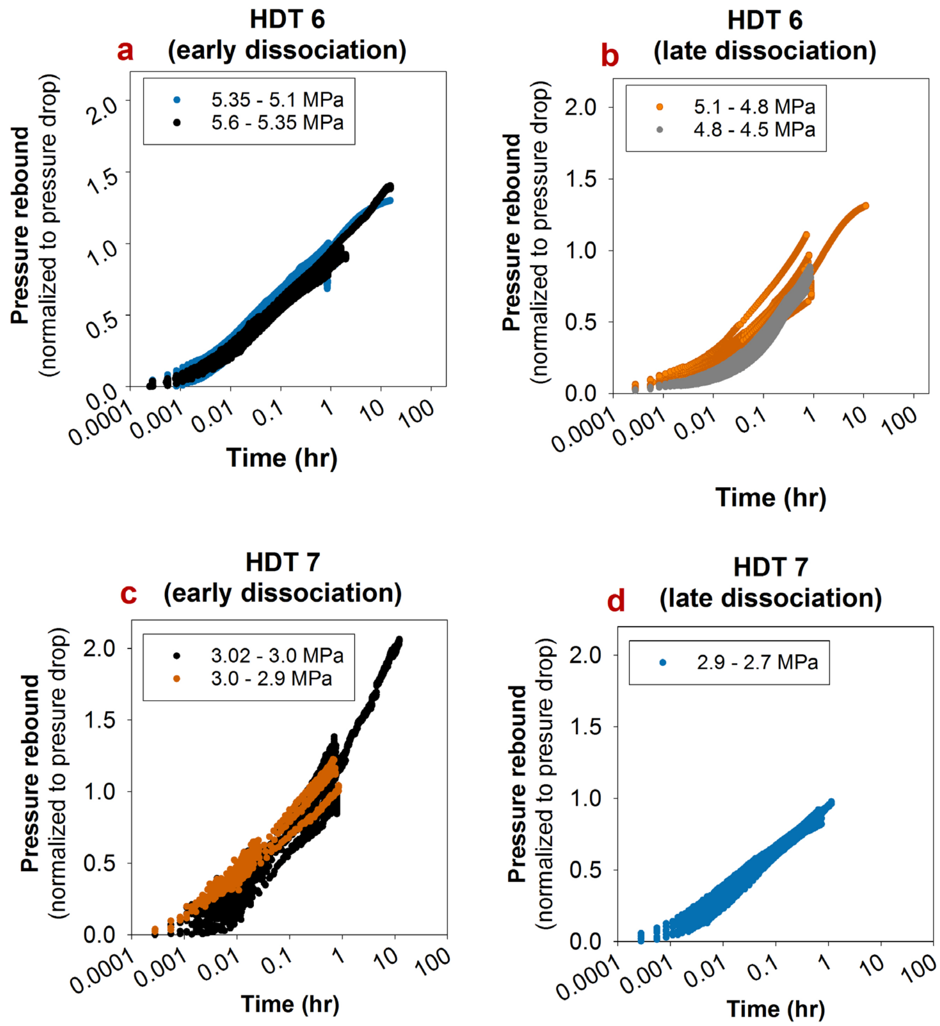

Figure 7.1: Comparison of pressure rebounds during shut-in for brine (HDT 6) and freshwater (HDT 7) experiments. These show the more concave-up behavior in late dissociation.

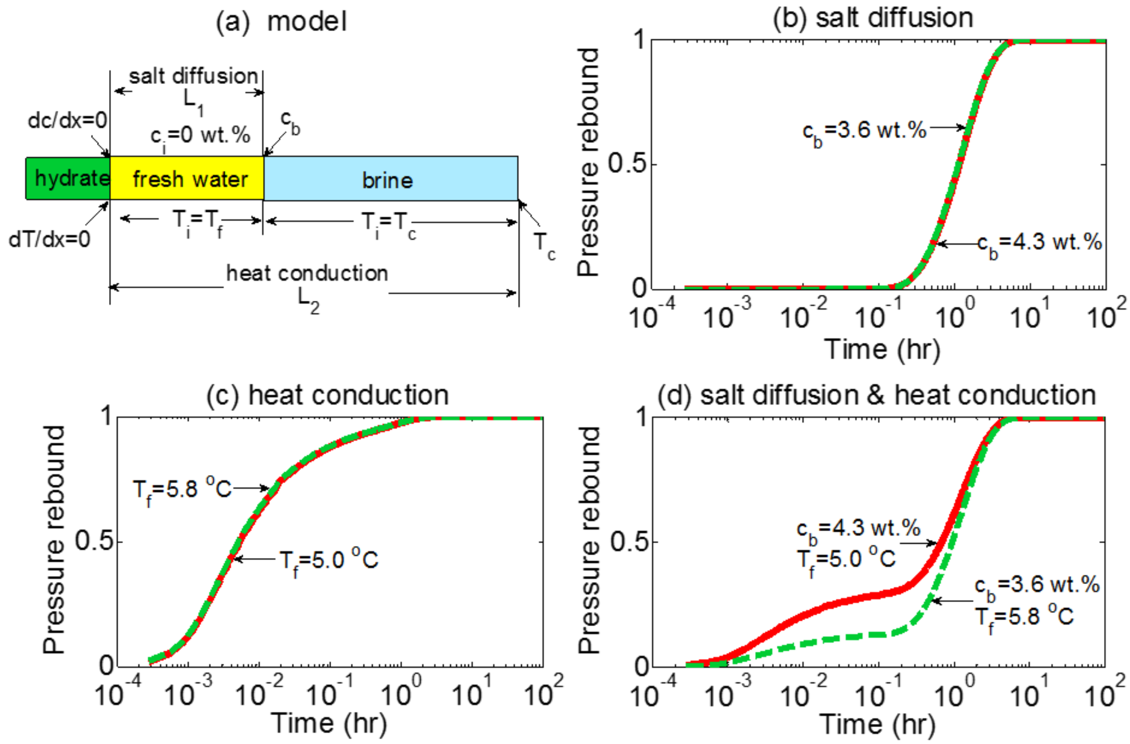

Figure 7.2: Modeling of salt and heat diffusion in the sand pack during dissociation when the sample is shut in. Only the combined effects of salt and heat diffusion (d) can show a general pattern such as observed in our samples.

We are continuing to work on processing CT data (example in Fig. 7.3) from a previous dissociation experiment to be able to observe bulk density changes over time during dissociation. These scans will help us look at the distribution of gas in the sample and possible flow during the depressurization process.

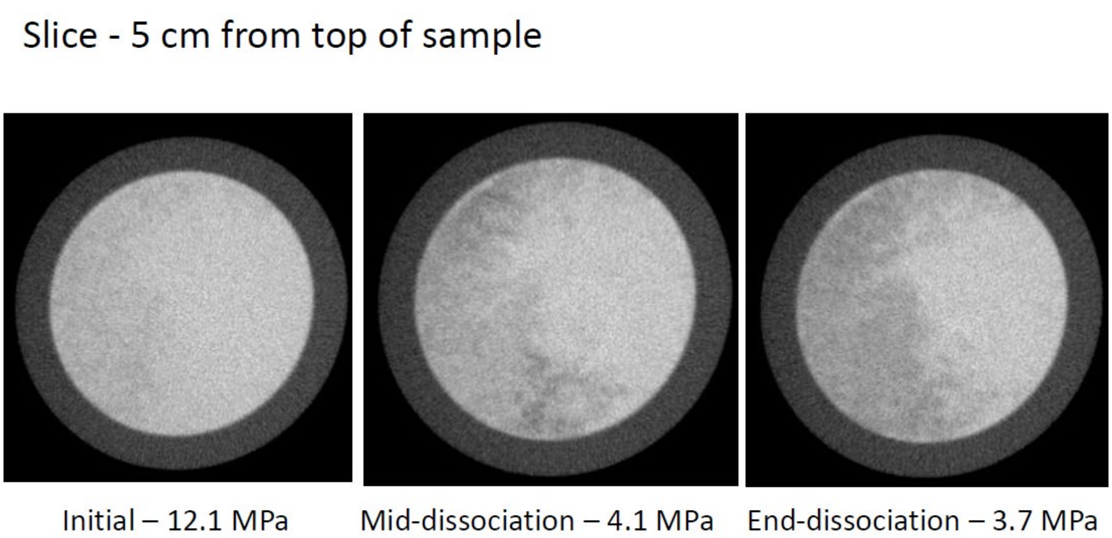

Figure 7.3: CT scans from three stages of dissociation of experiment HDT-8. Dark areas indicate a decrease in density due to an increase in gas saturation.

[Link to actions for next Quarter, Task 7](#)

Subtask 7.2 Depressurization of intact pressure cores

Planned Finish: 9/30/19
Actual Finish: In Progress

We depressurized 1 additional core section recovered from the northern Gulf of Mexico Green Canyon 955 during UT-GOM2-1. We are continuing to depressurize lithofacies-specific samples from uncompromised cores that have never left the hydrate stability field. During dissociation, we allowed for recovery and monitoring of pressure between degassing steps in the same manner as our synthetic hydrate experiments. For this most recent sample we have an initial hydrate saturation estimate of 96% of the pore volume.

At this point we have depressurized 8 natural samples with long pressure rebound observations, including sections of high saturation sandy silts, low saturation clayey silts, and sections containing both of these lithofacies. We are continuing to analyze pressure rebound data to look at the nature of the pressure rebound both as a pressure versus time.

Link to actions for next Quarter, Task 7

Task 8.0 Micro-Scale: CT experiments on Gulf of Mexico Sand Packs

Subtask 8.1 GOM2 Sample Preparation for Micro-CT
Planned Finish: 1/17/19
Actual Finish: In Progress

We are testing coarse sand instead of GOM2 samples due to the inability of our device to capture submicron pore geometries. A detailed rational was provided in the previous quarterly report.

Link to actions for next Quarter, Task 8

Subtask 8.2 Production Testing on GOM2 Samples Observed with Micro-CT
Planned Finish: 9/30/19
Actual Finish: In Progress

During this quarter we have conducted a methane hydrate formation experiment in excess-water condition monitored by time-lapse X-ray microtomography. The experiment uses Ottawa sand with rounded grains and ~700 μm median grain diameter instead of GOM sediments (See previous quarterly report). The experiment follows a pressure-temperature path into the methane hydrate stability zone as shown in **Fig. 8.1**.

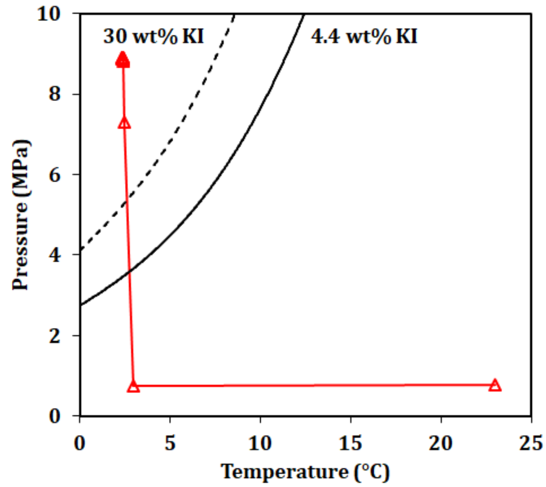

Fig. 8.1. Pressure-temperature path for excess-water experiment #1. Methane hydrate stability curves are given for 4.4 wt% and 30 wt% NaBr brine according to Tishchenko et al. 2005.

Sand is packed at 41% porosity. Methane gas is initially loaded at 23°C and 0.79 MPa. The temperature is decreased to 2.5°C and pressure brought up to 8.9 MPa (by injecting 4.4 wt% KI brine) to induce hydrate formation. Water injection results in a clear "water table", and high brine saturation at the bottom and low brine saturation on the top (**Fig. 8.2**). The micro-CT images reveal the hydrate-bearing sand-pack structure. Ordered according to CT number, the images show: aluminum vessel and spacer (white), sand (light gray), hydrate (dark gray), and methane gas (black). Brine CT number varies with salinity, from white (concentrated brine) to light gray (dilute brine 4.4 wt% KI). The pore space filled with gas above the "water table" gradually fills with hydrate (**Fig. 8.2**). Hence, most of the methane hydrate accumulates in the pore space near the top of the vessel.

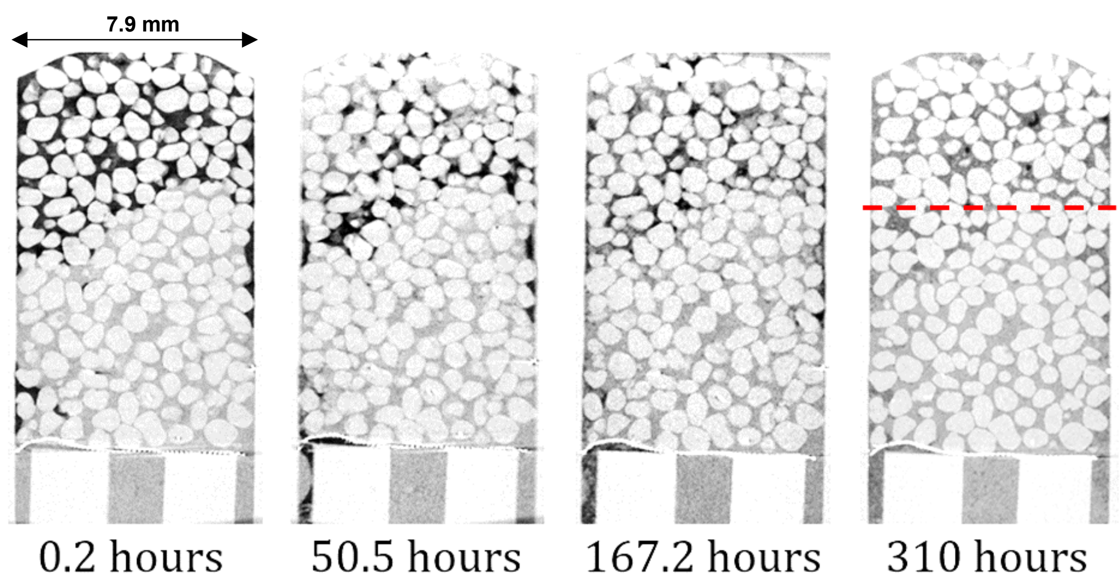

Fig. 8.2. Axial slices of micro-CT images taken for hydrate experiment in excess-water conditions. The vessel diameter is 7.9 mm. Color code: Aluminum vessel and spacer (white), sand (light gray), hydrate (dark gray), and methane gas (black). Brine CT number varies with salinity, from white (concentrated brine) to light gray (dilute brine 4.4 wt% KI).

Hydrate formation gradually exclude ions from the KI brine. The phenomenon is observed as increasing darkness in the hydrate pixels (**Fig. 8.3**). The segmented images help recognize the presence of hydrate in the pore space. Notice that water moves continually upwards because of methane gas conversion to hydrate. Similarly, to excess-gas experiments, we observe a few instances of local brine salinity increase by water withdrawal from neighboring hydrate.

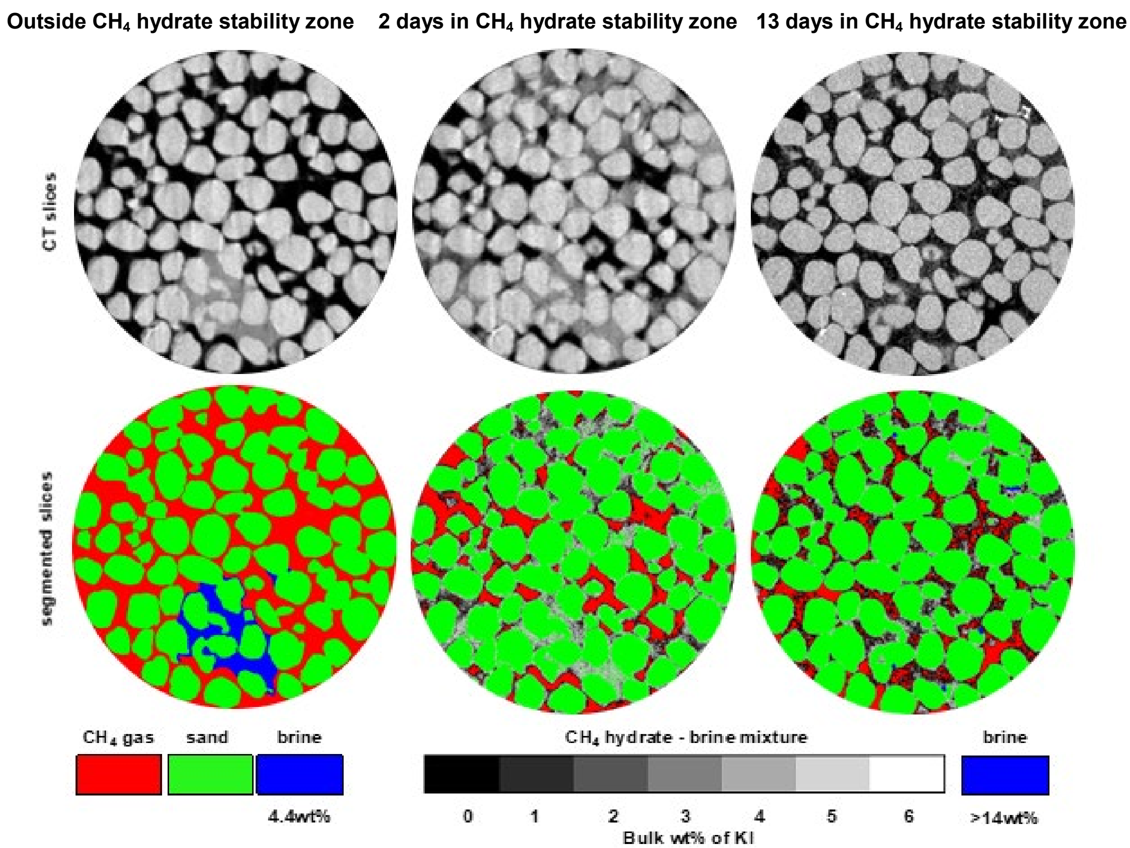

Fig. 8.3. Micro-CT and segmented slices with salinity calculation showing evolution of KI wt% in brine and brine-hydrate mixtures for excess-water experiment #1. The slices are taken near the height indicated in Fig. 8.2. The images show pore-filling hydrate mixed with brine that evolve into separate porous hydrate and high salinity brine phases.

We will perform a production test in this sample during the current quarter by depressurization.

Link to actions for next Quarter, Task 8

Task 9.0 Micro-Scale: Raman Observation on hydrate-bearing sand packs

Subtask 9.1 2D Imaging of methane hydrate sandpacks
Planned Finish: 3/31/2019
Actual Finish: 3/31/2019

We analyzed the Raman mapping data for our hydrate formation and dissociation experiment RH010 (detailed in previous reports) to understand how grain sizes influence the distribution of CH_4 hydrates in adjacent course- and fine-grained layers (Fig. 9.1). In this experiment, sandy silt and clay-free natural sands with different grain size distributions were loaded adjacently into the sample chamber, which ensured identical pressure-temperature conditions in these samples. The sandy silt sample was from core GC955-H005-06FB-2 (Lithofacies 2) at a depth of 429.46 - 429.56 meter below sea floor. The natural sands had diameters ranging from 200 μm to 300 μm, while the distribution of grain sizes of Lithofacies 2 showed a dominant peak at ~ 60 μm. Both CH_4 gas and brine with 3.5 wt.% NaCl were loaded into the sample chamber and CH_4 hydrates formed at ~ 15.5 MPa and 280 K. The temporal evolution of hydrate distribution was derived from the intensities of CH_4 Raman peaks in hydrates from the 2D Raman mappings (Fig. 9.2). During hydrate crystallization, comparable amounts of hydrates form in the Lithofacies 2 and Sand layers (Fig. 9.2.a). In later stages, less hydrates stayed in the Lithofacies 2 layer but concentrated in the coarser sand layer. The amount of time from first formation of hydrate until the hydrate fractions in each layer reached a plateau was about 10 days (Fig. 9.3). This grain-size controlled distribution of hydrate saturation can be at least partly explained by the higher CH_4 solubility in Lithofacies 2 due to its higher capillary pressure. We will develop a quantitative model to explain our observation in the upcoming quarter.

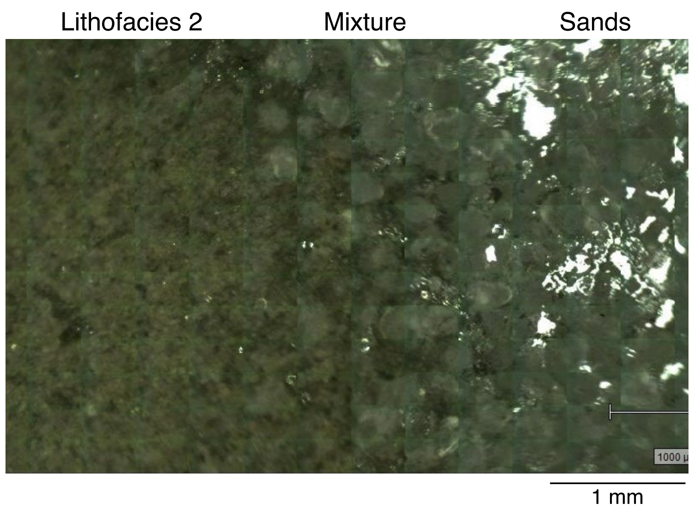

Figure 9.1. Optical image shows the sample loading in experiment RH010. From the left to the right, the two sections are sandy silt from core GC955-H005-06FB-2 (Lithofacies 2, mean diameter ~ 60 μms) and natural sands with diameters ranging from 200 – 300 μm.

Dissolved CH_4

cies 2

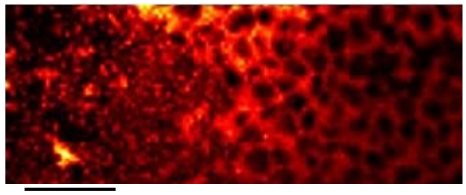

Figure 9.2. 2D Raman mappings show the spatial and temporal evolution of CH_4 hydrate distribution in adjacent Lithofacies 2 and sand layers. Along with time, hydrate content decreases in Lithofacies 2 but increases in sand layer (left column); the Lithofacies 2 layer has higher dissolved CH_4 content than the sand layer (right column).

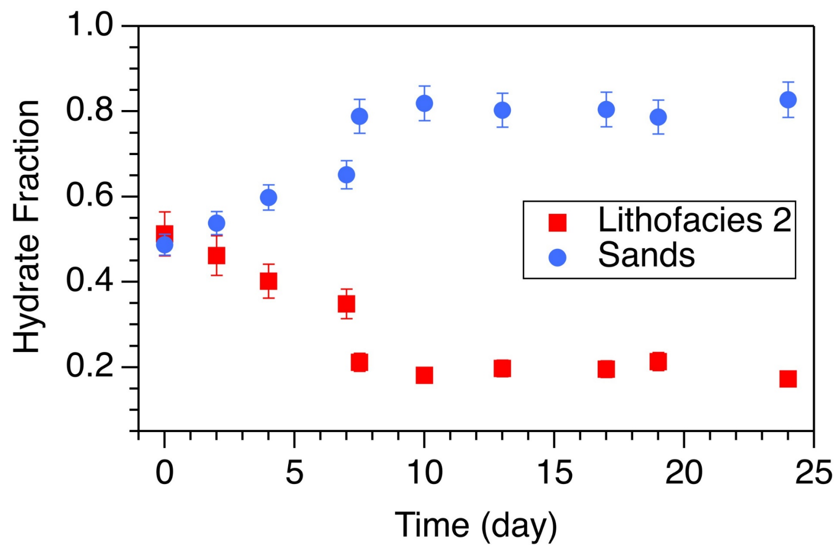

Figure 9.3. The temporal evolution of hydrate fractions in adjacent Lithofacies 2 and sand layers. The red squares and blue circles are the hydrate fractions in Lithofacies 2 and sand layers, respectively.

[Link to actions for next Quarter, Task 9]

Subtask 9.2 Micro-Raman Imaging of methane hydrate sandpacks
Planned Finish: 9/30/19
Actual Finish: In Progress

We finished a methane hydrate formation experiment (RH011), analogous to a previous experiment (RH009), but in a finer type of glass beads. The major motivations of doing this experiment are twofold: (1) to capture detailed Raman mapping data within 48 hours following the initial methane hydrate formation, (2) to repeat the experiment and test reproducibility. We used Raman spectrometer to map an area of 3000 µm by 3000 µm with a step size of 25 µm throughout the entire course of the experiment. Raman spectra were curve-fitted to derive large- to small-cage Raman peak area ratios. A ratio of 3 indicates thermodynamically structure-I (sI) methane hydrate and a ratio of 0.5 represents the thermodynamically unstable but kinetically preferred structure-II (sII) methane hydrate.

The results are remarkably similar to those of the previous experiment (RH009). Contrary to conventional understanding, the thermodynamically stable phase sI methane hydrate does not immediately form. Neither does the kinetically preferred sII hydrate. Instead, a mixture of sI methane hydrate and nonstoichiometric methane hydrate forms. Raman mappings reveals that the stoichiometry of methane hydrate is heterogeneous in space. 14 hours after the initial hydrate formation, a concentrated sI methane is seen, indicated by data points along the slope of 3 in Figure 9.4. Over a long time, the thermodynamics eventually drives the methane hydrate to its thermodynamic equilibrium, that is, sI methane hydrate. At 912 hours, almost all methane hydrate are sI methane hydrate with a large- to small-cage ratio of 3.

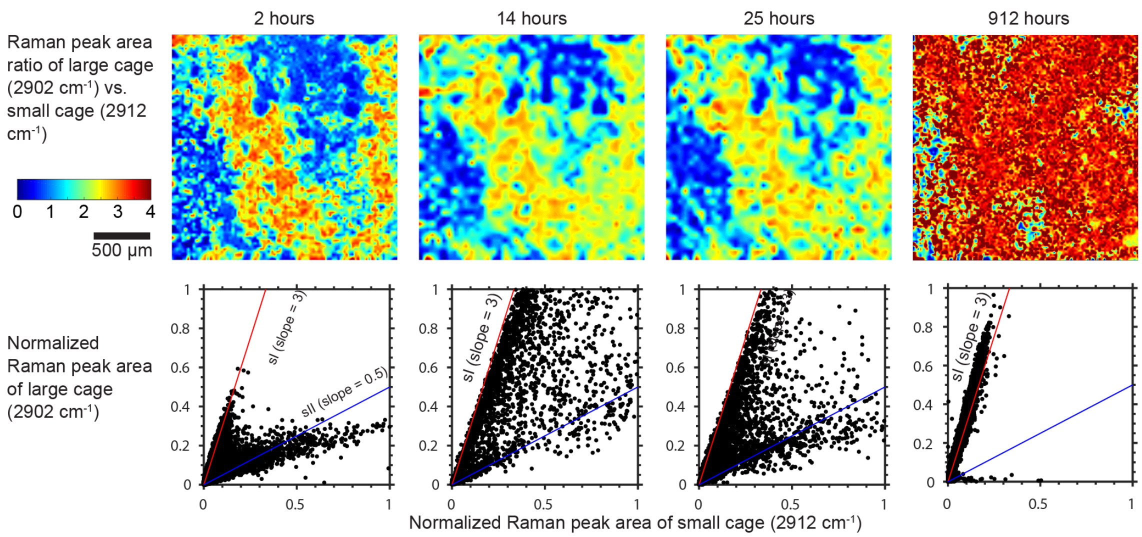

Figure 9.4. Raman 2D mapping and scatter plots of spatial and temporal distributions of methane hydrate large-peak to small-peak area ratios. Timestamps are zeroed at the initial methane hydrate formation. 2 hours after the initial methane hydrate formation, most of the methane hydrate formed is nonstoichiometric, meaning that it does not have a large- to small-cage ratio of 3. Over time, the methane hydrate system converges to its thermodynamic equilibrium, represented by sI methane hydrate with a large-to small- peak ratio of 3 at 912 hours.

Link to actions for next Quarter, Task 9

C. What opportunities for training and professional development has the project provided?

We provided technical training and mentoring to 1 high school student and two early college-age students. These students participate in experimental design, research meetings, and experimental measurements. We continue to train 2 doctoral students and 2 post-doctoral scientists. A third post-doctoral scientist trained on this and other projects was recently promoted to Research Associate.

D. How have the results been disseminated to communities of interest?

- A presentation was made at the Third Deep Carbon Observatory International Science Meeting, St. Andrews, Scotland, 23-25, March.
- A poster was presented at the 9th International Conference on Gas Hydrates, June 25-30, 2017, Denver, CO.
- A poster was presented at the American Geophysical Union Fall Meeting 2017, Dec. 11-15, 2017, New Orleans, LA.
- An invited talk was given at the American Geophysical Union Fall Meeting 2017, December 11-15, 2017, New Orleans, LA.
- Two posters were presented at the Gordon Research Conference- Natural Gas Hydrate Systems, 2018, Feb 25 – March 2, Galveston, TX
- Steve Phillips presented an update on HP3 at the DOE Mastering the Subsurface Through Technology Innovation, Partnerships, and Collaboration: Carbon Storage and Oil and Natural Gas Technologies Review Meeting in August 2018 in Pittsburgh, PA.
- A poster was presented at the American Geophysical Union Fall Meeting 2018, Dec. 10-14, in Washington DC, titled “X-Ray Micro-CT Observation of Methane Hydrate Growth in Sandy Sediments”
- A presentation was made at the American Geophysical Union Fall Meeting 2018, Dec. 10-14, 2018, in Washington DC, titled “Pore-Scale Methane Hydrate Formation under Pressure and Temperature Conditions of Natural Reservoirs”
- A poster was presented at the American Geophysical Union Fall Meeting in December 18, 2018, in Washington, D.C. titled “Three phase relative permeability of hydrate bearing sediments.”
- A poster was presented at the 8th Jackson School Research Symposium, February 2, 2019, in Austin, TX, titled “Pore-Scale Methane Hydrate Formation Under Pressure and Temperature Conditions of Natural Reservoirs”
- A poster was presented at the Austin Geological Society Research Symposium, April 1, 2018, in Austin, TX, titled “Pore-Scale Methane Hydrate Formation Under Pressure and Temperature Conditions of Natural Reservoirs”

E. What do you plan to do during the next reporting period to accomplish the goals?

Task 1.0 Project Management and Planning (next quarter plans)

Planned Finish: 09/30/19
Actual Finish: In progress

- Complete the Y3Q2 Quarterly
- Update the HP3 Website

Task 2.0 Macro-Scale: Relative Permeability of Methane Hydrate Sand Packs

Subtask 2.1 Laboratory Creation of Sand-Pack Samples at Varying Hydrate Levels
Planned Finish: 6/27/17
Actual Finish: 6/27/17

Subtask 2.2 Steady-State Permeability of Gas and Water of Sand-Pack Hydrate Samples
Planned Finish: 3/27/18
Actual Finish: 3/27/18

Task 3.0 Macro-Scale: Depressurization of Methane Hydrate Sand Packs

Subtask 3.1 Depressurization Tests
Planned Finish: 6/27/17
Actual Finish: 6/27/17

Subtask 3.2 Depressurization Tests with CAT scan
Planned Finish: 3/27/18
Actual Finish: 3/27/18

Task 4.0 Micro-Scale: CT Observation of Methane Hydrate Sand Packs

Subtask 4.1 Design and Build a Micro-CT compatible Pressure Vessel
Planned Finish: 6/27/17
Actual Finish: 6/27/17

Subtask 4.2 Micro-Scale CT Observations and Analysis
Planned Finish: 3/27/18
Actual Finish: 3/27/2018

Task 5.0 Micro-Scale: Raman Observation of Methane-Gas-Water Systems

Subtask 5.1 Design and Build a Micro-Raman compatible Pressure Vessel
Planned Finish: 6/27/17
Actual Finish: 6/27/17

Subtask 5.2 Micro-scale petrochemistry
Planned Finish: 03/21/18
Actual Finish: 3/27/18

Subtask 5.2 Diffusion kinetics of methane release
Planned Finish: 03/27/18
Actual Finish: 3/27/18

Task 6.0 Macro-Scale: Relative Permeability of Methane Hydrate Sand Packs and Intact Pressure Core Samples (next quarter plans)

Subtask 6.1 Steady-State Relative Permeability Measurements of Sand-Pack Hydrate Samples
Planned Finish: 9/30/19
Actual Finish: In Progress,

Our immediate experimental plan is to form hydrate in our vessel at a low and high hydrate saturation (~10% and 40%) and measure the water relative permeability at each saturation with no gas present. Once we have collected this data, we will continue with our three-phase injection to see if the predicted relative permeability is valid for three-phase conditions. We will focus on developing a simple understanding of relative permeability in terms of where gas and hydrate are distributed within the pore system.

In the current relative permeability experiment, based on the CT results, we will start with a fully dry core then slowly inject water into the core until we reach our desired water saturation. The flow rates must be quite slow (~0.1 ml/min or less) to get a homogenous distribution. Once we have our saturated core, we will form hydrates using the excess gas method. Once hydrates have been formed, we will scan our entire core at the UT-CT facility to determine the phase saturations (water, gas, and hydrate).

For the Layered Sands experiment, we will next CT scan this sandpack to ensure homogeneity, and will then form hydrate using the excess water method. The excess water method involves forming hydrate by first injecting the dry sandpack with methane at 1000 psi, then pressurizing the vessel to 1800 psi using a constant brine supply, with a 2000 psi confining pressure. The excess water method will be tested first, as it can theoretically reach higher hydrate saturations than the excess gas method. After we have successfully formed hydrate in the homogeneous sandpack, a layered system will be developed with a 250-micrometer sand layer interbedded between 50 micrometer sands.

Subtask 6.2 Steady-State Relative Permeability Measurements of Intact Pressure Cores
Planned Finish: 9/30/19
Actual Finish:

We will start this task by 5/1/19. Since the K0 permeability chamber does not include pressure taps, it will be difficult to assess the relative permeability while correcting for the capillary end effect. However, we do plan to perform co-injection of brine and gas into intact pressure cores to compare the overall pressures and flow rates in comparison with our sand pack and sandstone experiments.

Task 7.0 Macro-Scale: Depressurization of Methane Hydrate Sand Packs and Intact Pressure Core Samples (next quarter plans)

Subtask 7.1 Depressurization of sand-pack hydrate samples
Planned Finish: 1/17/19
Actual Finish: In Progress

We will finish analysis of CT data from the HDT-8 experiment and interpret based on dissociation stage and pressure rebound.

Subtask 7.2 Depressurization of intact pressure cores
Planned Finish: 9/30/19
Actual Finish: In Progress

We will synthesize all the results and compare the pressure rebound behavior relative to the phase boundary across the range of lithofacies and hydrate saturations, as well as compare the natural samples to the synthetic experiments. We will look at the influence of salinity, grain size, and hydrate saturation on rebound curves and

Task 8.0 Micro-Scale: CT experiments on Gulf of Mexico Sand Packs (next quarter plans)

During the last three quarters of this project we will focus on the observation of methane hydrate, brine and gas habit in sands, and hydrate pore habit varies upon dissociation and production. Our available technology cannot distinguish hydrate from brine in the pore space of sandy silts. Instead we will continue with the understanding and quantification of relative permeabilities in coarse sands.

Subtask 8.1 GOM2 Sample Preparation for Micro-CT

Planned Finish: 1/17/19
Actual Finish: In Progress

We propose to use the following sands instead of GOM2 sediments:

- the coarse sand we have been used for Task 4 (Ottawa sand with rounded grains and ~700 μm median grain diameter), and
- a fine sand with grain size ranging from 210 μm to 297 μm used in Task 9.

These results will be compared to the core-scale measurements of GOM2 samples.

Subtask 8.2 Production Testing on GOM2 Samples Observed with Micro-CT
Planned Finish: 9/30/19
Actual Finish: In Progress

- We will continue with the analysis of two methane hydrate dissociation experiments already performed. These experiments had originally just a small amount of hydrate and started from excess gas conditions.
- We will form methane hydrate in coarse sands with the water-excess method and monitor dissociation with time-lapse X-ray tomography.

Task 9.0 Micro-Scale: Raman Observation on hydrate-bearing sand packs (next quarter plans)

During the last three quarters of this project we will focus on investigating the role of porous media of different sizes that mimic the conditions of GOM2 Lithofacies 2 and 3, on the formation and dissociation of hydrates. This will be achieved through systematic studies of methane hydrate formation and dissociation in glass beads, natural quartz sand, and lithofacies 2 and 3. We will collaborate with Dr. Kehua You on numerical modelling of the physical processes (methane diffusion, capillary effect in porous media, length and time scale) to provide physical parameter constraints for understanding GOM2 reservoir.

Subtask 9.1 2D Imaging of methane hydrate sandpacks
Planned Finish: 6/30/19
Actual Finish: In Progress

- We will pursue the cylindrical sapphire tube design to explore methane hydrate formation and dissociation under pressure and flow gradients.
- We will develop a quantitative model to understand how grain sizes influence hydrate saturation.

Subtask 9.2 Micro-Raman Imaging of methane hydrate sandpacks
Planned Finish: 6/30/19
Actual Finish: In Progress

- We will assemble an experiment (RH012) similar to experiment RH010, but using glass beads with different grain sizes (200-300 μm vs. 40-50 μm). Such experimental configuration would avoid the strong Raman fluorescence signal from Lithofacies 2, as observed in experimental RH010. This will help us to better constrain the effect of grain sizes on hydrate distribution.

2. PRODUCTS:

What has the project produced?

a. Publications, conference papers, and presentations

Dong, T., Lin, J. F., Flemings, P. B., Polito, P. J. (2016), Pore-scale study on methane hydrate dissociation in brine using micro-Raman spectroscopy, presented at the 2016 Extreme Physics and Chemistry workshop, Deep Carbon Observatory, Palo Alto, Calif., 10-11 Dec.

Lin, J. F., Dong, T., Flemings, P. B., Polito, P. J. (2017), Characterization of methane hydrate reservoirs in the Gulf of Mexico, presented at the Third Deep Carbon Observatory International Science Meeting, St. Andrews, Scotland, 23-25, March.

Phillips, S.C., You, K., Flemings, P.B., Meyer, D.W., and Dong, T., 2017. Dissociation of laboratory-synthesized methane hydrate in coarse-grained sediments by slow depressurization. Poster presented at the 9th International Conference on Gas Hydrates, June 25-30, 2017, Denver, CO.

Chen, X., Espinoza, N., Verma, R., and Prodanovic, M. X-Ray Micro-CT Observations of Hydrate Pore Habit and Lattice Boltzmann Simulations on Permeability Evolution in Hydrate Bearing Sediments (HBS). Presented at the 2017 AGU Fall Meeting, December 11-15, 2017, New Orleans, LA.

Chen, X., & Espinoza, D. N. (2018). Ostwald ripening changes the pore habit and spatial variability of clathrate hydrate. Fuel, 214, 614–622. https://doi.org/10.1016/j.fuel.2017.11.065

Chen, X., Verma, R., Nicolas Espinoza, D., & Prodanović, M. (2018). Pore-Scale Determination of Gas Relative Permeability in Hydrate-Bearing Sediments Using X-Ray Computed Micro-Tomography and Lattice Boltzmann Method. Water Resources Research, 54(1), 600-608. https://doi.org/10.1002/2017WR021851

Chen, X and Espinoza, DN (2018), Surface area controls gas hydrate dissociation kinetics in porous media, Fuel, 234, 358-363. https://doi.org/10.1016/j.fuel.2018.07.030

Chen X, D. Nicolas Espinoza, Nicola Tisato, Peter B. Flemings (2018). X-ray Computed Micro-Tomography Study of Methane Hydrate Bearing Sand: Enhancing Contrast for Improved Segmentation, Gordon Research Conference – Natural Gas Hydrate Systems, Galveston, TX

Chen X, D. Nicolas Espinoza, Nicola Tisato, Rahul Verma, Masa Prodanovic, Peter B. Flemings, (2018). New Insights Into Pore Habit of Gas Hydrate in Sandy Sediments: Impact on Petrophysical and Transport Properties, Gordon Research Conference – Natural Gas Hydrate Systems, Galveston, TX

Chen X, D. Nicolas Espinoza, Nicola Tisato, Peter B. Flemings (2018). "X-Ray Micro-CT Observation of Methane Hydrate Growth in Sandy Sediments", American Geophysical Union Fall Meeting 2018, Dec. 10-14, in Washington DC.

Dong, T., Lin, J.-F., Flemings, P.B., Gu, J.T., Liu, J., Polito, P.J., O'Connell, J. (2017) Pore-scale study on gas hydrate formation and dissociation under relevant reservoir conditions of the Gulf of Mexico, presented at the 2017 Extreme Physics and Chemistry workshop, Deep Carbon Observatory, November 4-5, Tempe, AZ.

Dong, T., Lin, J.-F., Gu, J.T., Polito, P.J., O'Connell, J., Flemings, P.B. (2017), Spatial and temporal dependencies of structure II to structure I methane hydrate transformation in porous media under moderate pressure and temperature conditions, Abstract OS53B-1188 Presented at 2017 Fall Meeting, December 11-15, New Orleans, LA.

Dong, T., Lin, J.-F., Gu, J.T., Polito, P.J., O'Connell, J., Flemings, P.B. (2018), Transformation of metastable structure-II to stable structure-I methane hydrate in porous media during hydrate formation, poster presented at 2018 Jackson School of Geosciences Symposium, Feb. 3, 2018, Austin, TX.

Dong, T., Lin, J.-F., Flemings, P.B., Gu, J.T., Polito, P.J., O'Connell, J. (2018), Pore-scale methane hydrate dissociation in porous media using Raman spectroscopy and optical imaging, poster presented at Gordon Research Conferences on Natural Gas Hydrate Systems, Feb. 25-March 2, 2018, Galveston, TX.

Dong, T., Lin, J.-F., Flemings, P.B., Gu, J.T., Polito, P.J., O'Connell, J. (2018), Pore-Scale Methane Hydrate Formation under Pressure and Temperature Conditions of Natural Reservoirs, American Geophysical Union Fall Meeting 2018, Dec. 10-14, 2018, Washington DC.

Meyer, D.W., Flemings, P.B., DiCarlo, D., You, K., Phillips, S.C., and Kneafsey, T.J. (2018), Experimental investigation of gas flow and hydrate formation within the hydrate stability zone. Journal of Geophysical Research- Solid Earth https://doi.org/10.1029/2018JB015748

Meyer, D., Flemings, P.B., DiCarlo, D. (submitted), Effect of Gas Flow Rate on Hydrate Formation Within the Hydrate Stability Zone, Journal of geophysical research

Meyer, D., PhD Dissertation (submitted) Dynamics of Gas Flow and Hydrate Formation within the Hydrate Stability Zone

Murphy, Z., Fukuyama, D., Daigle, H., DiCarlo, D. (2018), Three-phase relative permeability of hydrate-bearing sediments, poster presented at the American Geophysical Union Fall Meeting, Dec. 10-14, 2018, Washington, D.C.

Phillips, S.C., Flemings, P., You, K., Meyer, D., and Dong, T., in review. Investigation of in situ salinity and methane hydrate dissociation in coarse-grained sediments by slow, stepwise depressurization.

b. Website(s) or other Internet site(s)

- Project SharePoint: https://sps.austin.utexas.edu/sites/GEOMech/HP3/_layouts/15/start.aspx#/SitePages/Home.aspx
- Project Website

  https://ig.utexas.edu/energy/hydrate-production-properties/

c. Technologies or techniques

Nothing to Report.

d. Inventions, patent applications, and/or licenses

Nothing to Report.

e. Other products

Research Performance Progress Report (Period ending 12/31/16)
Research Performance Progress Report (Period ending 3/31/17)
Research Performance Progress Report (Period ending 6/30/17)
Research Performance Progress Report (Period ending 9/30/17)
Research Performance Progress Report (Period ending 12/31/17)
Research Performance Progress Report (Period ending 3/31/18)
Phase 1 Report (Period ending 3/31/18)
Research Performance Progress Report (Period ending 6/30/18)
Research Performance Progress Report (Period ending 9/30/2018)
Research Performance Progress Report (Period ending 12/31/2018)

3. CHANGES/PROBLEMS:

This section highlights changes and problems encountered on the project.

a. Changes in approach and reasons for change

- Relative Permeability Experiments (Task 6): Since the K0 permeability chamber for measuring intact pressure cores does not include pressure taps, determining accurate relative permeabilities to the gas phase will not be possible because of an unknown degree of capillary end effect. We do plan to continue with co-injection of gas and brine into intact pressure cores, but only as a method of comparison with our sand pack and sandstone results in terms of overall pressure drop and flow rate.

- Microscale Imaging (Task 8): Our available technology is insufficient to clearly distinguish hydrate and brine and observe hydrate pore habit in Lithofacies 2 of GOM2. With such small pore sizes (<1 μm), it would be extremely difficult to segment pore space and hydrate in these silts even doing scans with a high-resolution X-ray micro-tomograph. For this reason, we consulted with the DOE project manager R. Baker and proposed to concentrate our microCT efforts for the remainder of the project on coarser sediments in which we can distinguish CH_4 hydrate clearly. Our plan is to continue to image pore habit of methane hydrate and to analyze its effect on relative permeability as planned in subtasks 8.1 and 8.2. However, we will use coarser sediments that allow for hydrate/brine segmentation and permit using X-ray to its fullest.

- Micro-Raman (Task 9): The originally designed semi-cylindrical Flow-Thru Chamber cannot be produced after several attempts in accordance with sapphire specialist Rayotek Scientific Inc., due to technical difficulty. If time allows, we will pursue another design of the Flow-Thru Chamber: a cylindrical sapphire tube that is transparent to Raman imaging. In addition, we have developed a natural sediment chamber to receive samples for Mico-Raman directly from the Pressure Core Analysis and Transfer System (PCATS) that is now being tested.

b. Actual or anticipated problems or delays and actions or plans to resolve them

Nothing to Report.

c. Changes that have a significant impact on expenditures

Nothing to Report.

d. Change of primary performance site location from that originally proposed

Nothing to Report.

4. SPECIAL REPORTING REQUIREMENTS:

Special reporting requirements are listed below.

PAST - BUDGET PERIOD 1

Nothing to Report

CURRENT – BUDGET PERIOD 2

Nothing to Report.

5. BUDGETARY INFORMATION:

The Cost Summary is in Exhibit 1.

EXHIBIT 1 – COST SUMMARY

Baseline Reporting Quarter	Budget Period 1 (Year 1)							
	Q1		Q2		Q3		Q4	
	10/01/16-12/31/16		01/01/17-03/31/17		04/01/17-06/30/17		07/01/17-09/30/17	
	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total
Baseline Cost Plan								
Federal Share	$ 283,497	$ 283,497	$ 82,038	$ 365,535	$ 79,691	$ 445,226	$ 79,691	$ 524,917
Non-Federal Share	$ 170,463	$ 170,463	$ 7,129	$ 177,593	$ 7,129	$ 184,722	$ 7,129	$ 191,851
Total Planned	$ 453,960	$ 453,960	$ 89,167	$ 543,128	$ 86,820	$ 629,948	$ 86,820	$ 716,768
Actual Incurred Cost								
Federal Share	$ 6,749	$ 6,749	$ 50,903	$ 57,652	$ 67,795	$ 125,447	$ 162,531	$ 287,977
Non-Federal Share	$ 10,800	$ 10,800	$ 10,800	$ 21,600	$ 10,800	$ 32,400	$ 158,478	$ 190,878
Total Incurred Cost	$ 17,549	$ 17,549	$ 61,703	$ 79,252	$ 78,595	$ 157,847	$ 321,009	$ 478,855
Variance								
Federal Share	$ (276,748)	$ (276,748)	$ (31,135)	$ (307,883)	$ (11,896)	$ (319,779)	$ 82,840	$ (236,940)
Non-Federal Share	$ (159,663)	$ (159,663)	$ 3,671	$ (155,993)	$ 3,671	$ (152,322)	$ 151,349	$ (973)
Total Variance	$ (436,411)	$ (436,411)	$ (27,465)	$ (463,876)	$ (8,226)	$ (472,101)	$ 234,188	$ (237,913)

Baseline Reporting Quarter	Budget Period 1 & 2 (Year 2)							
	Q1		Q2		Q3		Q4	
	10/01/17-12/31/17		01/01/18-03/31/18		04/01/18-06/30/18		07/01/18-09/30/18	
	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total
Baseline Cost Plan								
Federal Share	$ 109,248	$ 634,165	$ 89,736	$ 723,901	$ 128,914	$ 852,815	$ 106,048	$ 958,863
Non-Federal Share	$ 7,342	$ 199,193	$ 19,369	$ 218,562	$ 7,342	$ 225,904	$ 31,393	$ 257,297
Total Planned	$ 116,590	$ 833,358	$ 109,105	$ 942,463	$ 136,256	$ 1,078,719	$ 137,441	$ 1,216,160
Actual Incurred Cost								
Federal Share	$ 107,216	$ 395,193	$ 154,758	$ 549,951	$ 163,509	$ 713,460	$ 161,083	$ 874,542
Non-Federal Share	$ 19,857	$ 210,735	$ 7,140	$ 217,875	$ 32,567	$ 250,442	$ 7,241	$ 257,683
Total Incurred Cost	$ 127,073	$ 605,928	$ 161,898	$ 767,826	$ 196,076	$ 963,902	$ 168,324	$ 1,132,225
Variance								
Federal Share	$ (2,032)	$ (238,972)	$ 65,022	$ (173,950)	$ 34,595	$ (139,355)	$ 55,035	$ (84,321)
Non-Federal Share	$ 12,515	$ 11,542	$ (12,229)	$ (687)	$ 25,225	$ 24,538	$ (24,152)	$ 386
Total Variance	$ 10,483	$ (227,430)	$ 52,793	$ (174,637)	$ 59,820	$ (114,817)	$ 30,883	$ (83,934)

Baseline Reporting Quarter	Budget Period 2 (Year 3)							
	Q1		Q2		Q3		Q4	
	10/01/18-12/31/18		01/01/19-03/31/19		04/01/19-06/30/19		07/01/19-09/30/19	
	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total
Baseline Cost Plan								
Federal Share	$ 80,035	$ 1,038,898	$ 53,698	$ 1,092,596	$ 53,698	$ 1,146,294	$ 53,695	$ 1,199,989
Non-Federal Share	$ 7,581	$ 264,878	$ 7,579	$ 272,457	$ 7,579	$ 280,036	$ 19,965	$ 300,001
Total Planned	$ 87,616	$ 1,303,776	$ 61,277	$ 1,365,053	$ 61,277	$ 1,426,330	$ 73,660	$ 1,499,990
Actual Incurred Cost								
Federal Share	$ 52,733	$ 927,275	$ 30,119	$ 957,394				
Non-Federal Share	$ 7,554	$ 265,237	$ 21,498	$ 286,735				
Total Incurred Cost	$ 60,287	$ 1,192,512	$ 51,617	$ 1,244,129				
Variance								
Federal Share	$ (27,302)	$ (111,623)	$ (23,579)	$ (135,202)				
Non-Federal Share	$ (27)	$ 359	$ 13,919	$ 14,278				
Total Variance	$ (27,329)	$ (111,264)	$ (9,660)	$ (120,924)				

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