NATIONAL ENERGY TECHNOLOGY LABORATORY
OIL & GAS

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Quarterly Research Performance Progress Report (Period Ending 6/30/2018)

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

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

Submitted by:
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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 third quarter of the second year in the second budget period. The majority of the progress made was starting work on the Phase 2 Milestones and completing the Phase 1 report.

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_Task_2.0_Macro-Scale:	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_Task_2.0_Macro-Scale:_1	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_Task_3.0_Macro-Scale:	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_Task_4.0_Micro-Scale:_1	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_Task_4.0_Micro-Scale:_1	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_Task_5.0_Micro-Scale:	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_Task_5.0_Micro-Scale:	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)_Task_6.0_Macro-Scale:_2_Task_6.0_Macro-Scale:_2	1/17/2019 (Y3Q2)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 6.1)	In progress
Milestone 2.B - Measurement of relative permeability in intact pressure cores. (See Subtask 6.2)_Task_6.0_Macro-Scale:_2_Task_6.0_Macro-Scale:_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) Task_7.0_Macro-Scale:_Task_7.0_Macro-Scale:	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) Task_8.0_Micro-Scale:_Task_8.0_Micro-Scale:	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) Task_9.0_Micro-Scale:_Task_9.0_Micro-Scale:	1/17/2019 (Y3Q2)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 9.1)	In progress
Milestone 2.F - 2D micro-Raman analysis of natural methane hydrate samples at depressurization; (See Subtask 9.1 and 9.2) Task_9.0_Micro-Scale:_Task_9.0_Micro-Scale:_1	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.

<u>CURRENT – BUDGET PERIOD 2</u>

Task 1.0 Project Management and Planning

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

This tasks continues from Phase 1.
The sixth Quarter Report was submitted on April 25, 2018.
The Phase 1 report was completed and submitted on June 20, 2018 to FITS and to OSTI (submission number 1454037)

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

The tasks for this quarter were to run relative permeability experiments for simultaneous flow of water and gas at a range of hydrate saturations. We have successfully generated synthetic hydrate in sand packs as well as high-permeability Boise and Berea sandstones, with initial hydrate saturations ranging from 20-40%. Two-phase relative permeability measurements have been performed on Boise sandstone with 24% hydrate saturation.

Process Improvements
Several process improvements have been made for better reproducibility. First, the transducer lines have been filled with 13% NaCl brine to prevent hydrate formation in the lines. Second, after hydrate formation has completed, we perform a pressure cycling procedure to homogenize the hydrate within the core. This is done by first decreasing the pore pressure of the brine phase to 100 psi lower than the three-phase stability pressure, followed by an increase to 100 psi above the three-phase stability pressure. These cycles are held for 12 hours and repeated for two days.

Results
Our process improvements have allowed us to successfully determine relative permeability to brine in the presence of hydrate. To find the relative permeability, we first determined the absolute permeability of the Boise sandstone with a single brine phase. We see a linear correlation between flow rate and pressure drop (Fig. 1), which we expect based on Darcy's law.

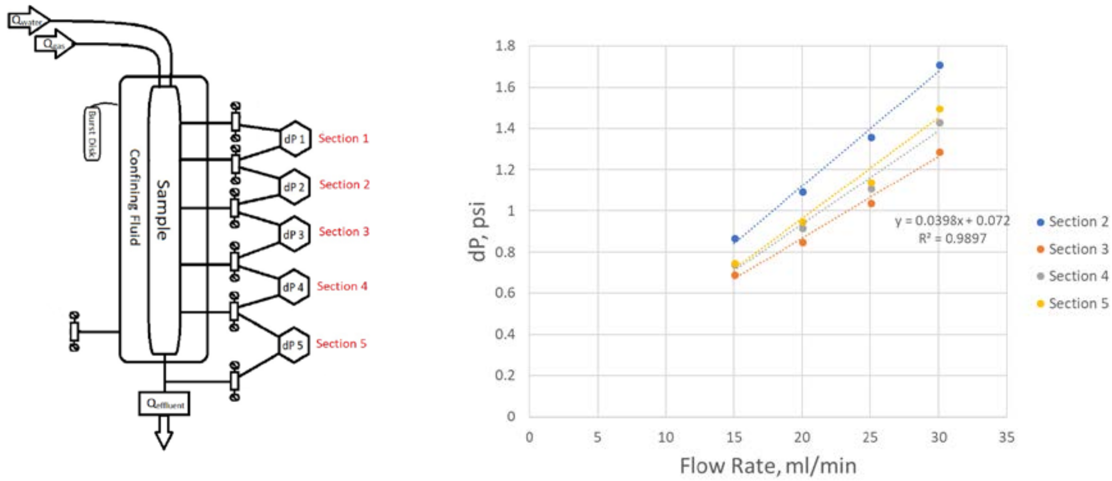

Figure 1. (A) Schematic of pressure core vessel with sections of core marked. **(B)** Pressure drop versus flow rate for a single phase (water) in the Boise sandstone core with no hydrate present.

From these values, we calculate absolute permeability (Table 1). The absolute permeability from the Boise sandstone range from 3.9 to 5.5 Darcy, which is consistent with literature values (Table 1).

Section	Permeability, Darcy
2	3.9
3	5.5
4	4.8
5	4.5

Table 1. Absolute permeability values for different sections of Boise sandstone. Variations are from the natural variations in the cross-bedded sandstone.

Following the absolute permeability measurements, we formed hydrate in the core, and performed our pressure cycling procedure. Using mass balance on the methane component we find that the hydrate saturation in this sample was 24%. We flowed 10.5% salinity brine (calculated to be the salinity for three-phase equilibrium for this pressure and temperature) through the core at flow rates ranging from 5 to 15 mL/min to measure two phase effective permeability and to ensure linear behavior (Fig. 2).

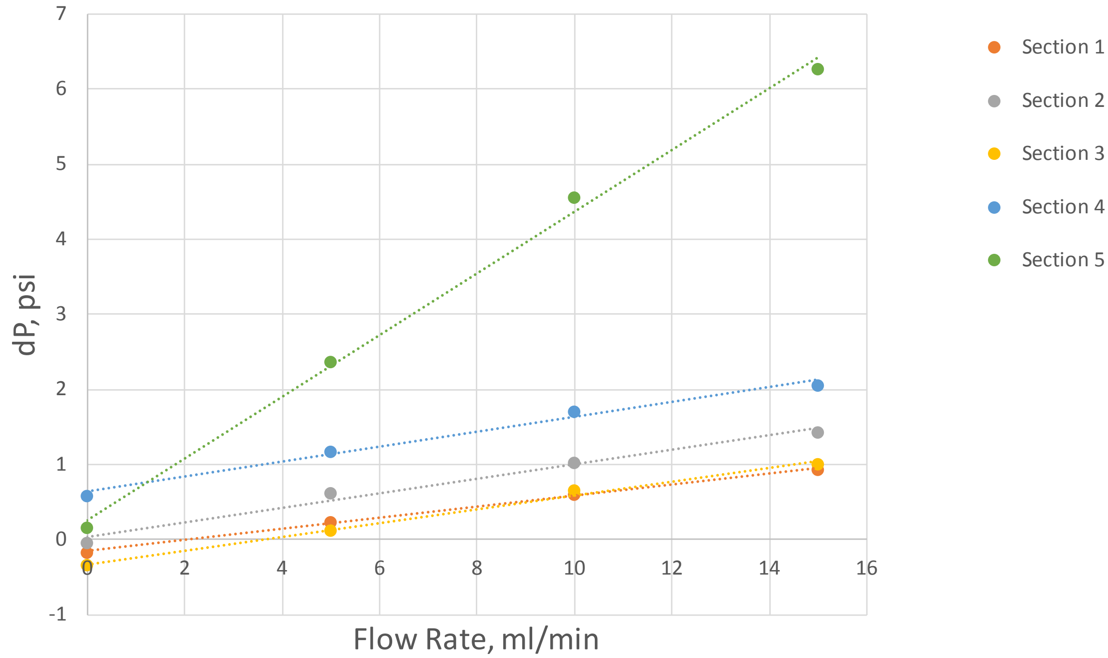

Figure 2. Pressure drop versus flow rate in the Boise sandstone core with 24% average hydrate saturation.

After confirming the linear relationship between pressure drop and flow rate, we calculated effective permeabilities of each section, as well as relative permeability (Table 2). Section 5 has a much lower permeability, which is likely due to end effects, and not a true representation of the permeability in that section. End effects are often seen in relative permeability experiments and are usually due to the fluids going from a region where there are capillary forces (inside the core) to where there are no capillary forces (outside the core). This can skew relative permeability measurements and is one of the reasons why we use pressure taps in the core to get a more accurate measurement from the center sections of the core.

Section	Absolute Permeability, Darcy	Effective Brine Permeability, Darcy	Brine Relative Permeability k_{rw}
1	4.7	3.0	0.64
2	3.9	2.3	0.58
3	5.5	2.4	0.43
4	4.8	2.2	0.46
5	4.5	0.53	0.12

Table 2. Effective and relative permeabilities to brine in each section of the Boise sandstone core with 24% hydrate saturation (S_w = 0.76). There is no free gas in the core.

Future work

Now that we have a reproducible method of forming hydrate and measuring two-phase relative permeability, we are conducting three-phase relative permeability measurements by flowing both brine and gas through the core at hydrate stability conditions. We have successfully performed gas/brine injections and measured pressure drops when the experiments are performed at room temperature. However, currently, we are having difficulties with brine and gas co-injection at hydrate forming conditions. We find that hydrate blockages form inside the system, which limits our ability to inject gas even if the brine is in the three-phase condition. After troubleshooting, we have isolated these blockages to the outlet where the back pressure regulator (BPR) maintains the pressure in the core. To eliminate these blockages, we will immerse the BPR in a warm water bath that should destroy any hydrate that has formed and prevent future formation.

By eliminating the hydrate blockages, we will be able to flow both gas and water through the core. We will measure pressure drops during co-injection and calculate permeability ratios (k_{rw}/k_0) for three-phase conditions. Once we are able to co-inject brine and gas in the presence of hydrate, we will measure relative permeability values for multiple injection ratios (Q_{gas}/Q_{water}) at a single hydrate saturation. After completing a relative permeability curve for a given hydrate saturation, we will form samples with different hydrate saturations and measure relative permeabilities for those samples.

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

We have begun preparing sand pack samples to be formed using the excess gas method of Task 2.0.

We revised and resubmitted a manuscript based on our depressurization experiments from Task 3.0 in sand packs containing hydrate formed with a gas injection method. 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 pressure rebounds. These results show that when hydrate dissociation begins, localized freshening and cooling around the hydrate sets up salinity and heat gradients that change the conditions around the dissociating hydrate. We are working to extend these observations to a larger range of hydrate saturations, using multiple hydrate formation methods, and in natural samples.

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 3 core sections recovered from the northern Gulf of Mexico Green Canyon 955 during UT-GOM2-1. In each depressurization we allowed for recovery and monitoring of pressure between degassing steps. We observe pressure at the manifold with a transducer and pressure and temperature in the degassing vessel (Fig. 7.1) using a data storage tags (DST). We observe pressure rebounds like those observed in synthetic samples in Task 3.0 that evolve in form during the course of dissociation (Fig. 7.2). We have depressurized compromised cores (cores that partially lost pressure and were possibly damaged during processing) to establish our depressurization method and will move on to lithofacies-specific samples in non-compromised cores.

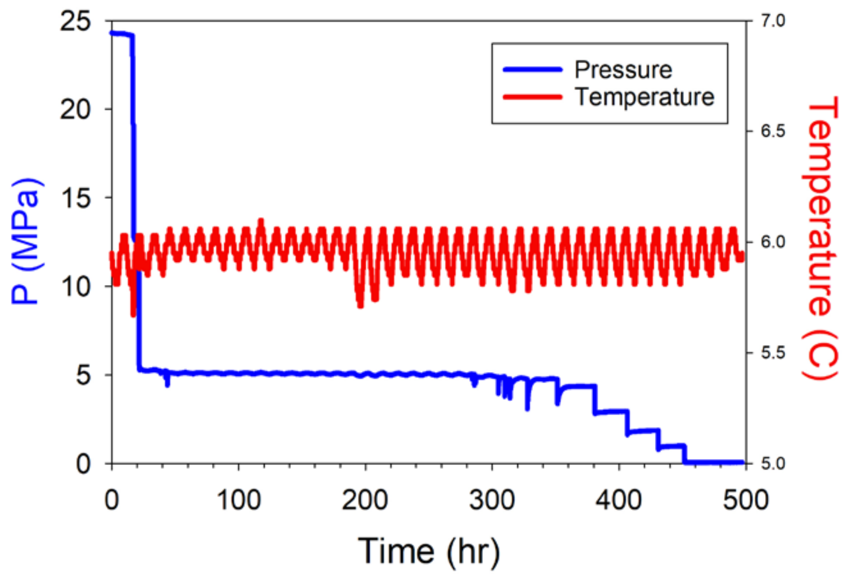

Figure 7.1. Pressure and temperature within the vessel in a depressurization of a hydrate-bearing sediment core from Green Canyon 955. Pressure rebounds result in a plateau in the time series of pressure. Changes in room temperature cause ~0.2 degree C variation in temperature in the vessel, with a slight change in pressure.

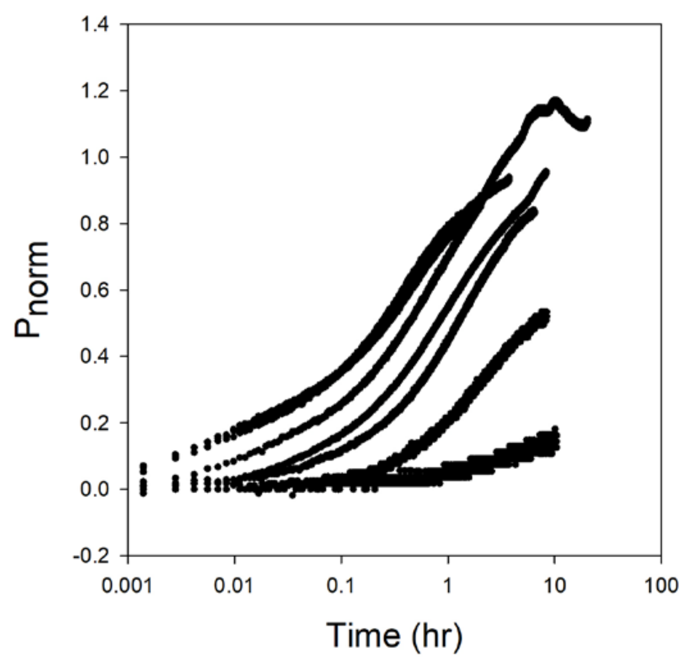

Figure 7.2. Normalized pressure rebounds (P_{norm}: the ratio of increase of pressure to the starting pressure before each gas release and pressure drop) versus the log of time for a high hydrate saturation (86%) pressure core sample from Green Canyon 955.

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

In the previous quarterly report, we have shown methane hydrate existence at the pore scale in coarse sand with micro-CT images. Yet, it was difficult to clearly segment between methane hydrate phase and brine phase in the micro-CT images without the help of mass balance equations. Hence, it is important to increase CT contrast between methane hydrate phase and brine phase, which is especially critical for imaging methane hydrate in fine sand, such as Gulf of Mexico sand from the GOM2 expedition.

The recent study by *Lei at el. (2018), Geophysical Research Letters,* has shown that, adding potassium iodide (KI) salts can significantly improve the phase segmentation between methane hydrate and brine from micro-CT imaging. The reason is that KI has a greater molecular weight than NaBr (used in our previous experiments) and can increase the X-ray attenuation for the brine phase.

In our new methane hydrate experiment, we partially saturate coarse sand (~700 µm median grain diameter) with 4.37 wt% KI brine at an initial water saturation of ~20% and methane gas at an initial pressure of 8.38 MPa (excess gas condition). The temperature and pressure change during the experiment and the pressure-temperature (PT) path in comparison with phase boundaries are shown in Fig. 8.1. Once the PT conditions cross the phase boundary, the experimental condition quickly shifts into the hydrate stability zone to induce hydrate formation.

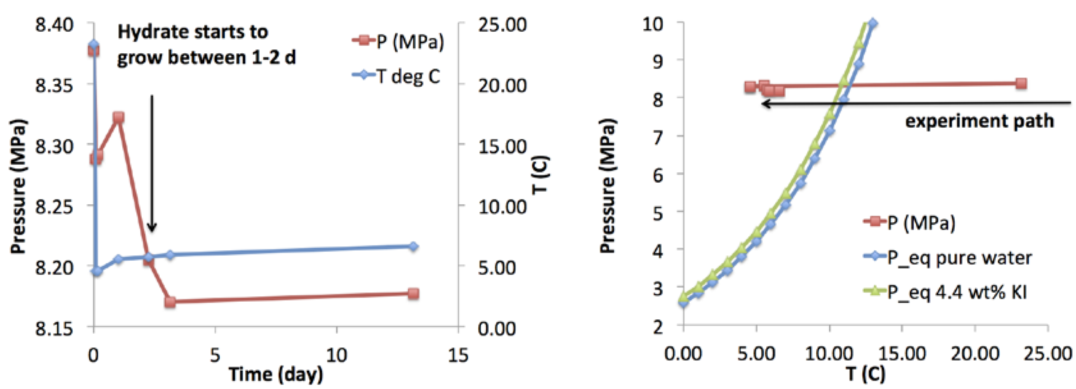

Figure 8.1 Left, times series of temperature and pressure during the experiment; right, the path of experimental temperature and pressure in comparison to hydrate phase boundaries with 4.37 wt% KI and no salt in the aqueous phase.

We do not measure methane hydrate formation within the first day after temperature decrease. The left column of Fig. 8.2 shows one micro-CT slice of sand after 1 day of temperature decrease and the corresponding CT grayscale histogram. In the CT image, we observe the concave curvatures of brine within sand grains, which is due to water-wet sand. By adding KI in brine, the grayscale number of brine increases and has some overlap with the sand peak in the histogram.

We clearly observe methane hydrate formation in the CT images after 2 days within the stability zone. The right column of Fig. 8.2 shows the CT slice at the same location 2 days after crossing the phase boundary. First, the CT image shows that methane hydrate phase displays a lower grayscale number than brine phase (on the left column) and methane hydrate occupies a distinct peak in the histogram that is away from both methane gas and sand (brine peak overlaps with the sand peak). Second, methane hydrate has convex curvatures towards the gas phase and irregular shapes. The two observations are clear CT evidence of methane hydrate existence in sand and facilitate straightforward phase segmentation for hydrate versus brine. We plan to start with this technique to image hydrate pore habit in Gulf of Mexico sands.

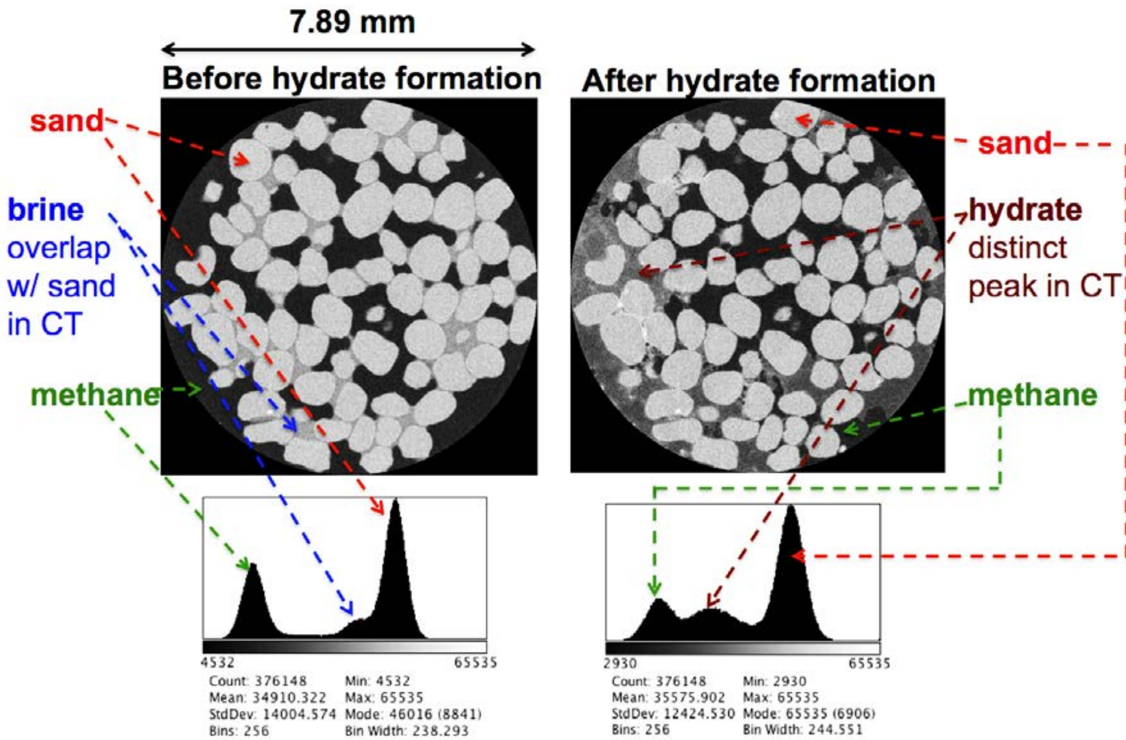

Figure 8.2 Left: micro-CT image of sand after 1 day within hydrate stability zone. Right: micro-CT image of sand at the same position after 2 days within hydrate stability zone (by increasing pressure first and lowering temperature later).

Fig. 8.3 shows a micro-CT image (resolution: 3.50 µm) of the Gulf of Mexico sandy-silt (Well GC 955 H005, lithofacies 2, depth 415-450m below sea floor) and the grain size distribution based on the CT image. Similar to the grain size distribution measured by laser particle analysis (data from UT-GOM2-1 Hydrate Pressure Coring Expedition Report, https://ig.utexas.edu/files/2018/02/1.0-UT-GOM2-1-Expedition-Summary.pdf), the CT measurement yields a median grain size of 40 µm. The grain size distribution from the CT image disregards grains smaller than 10 µm in diameter due to image resolution limits.

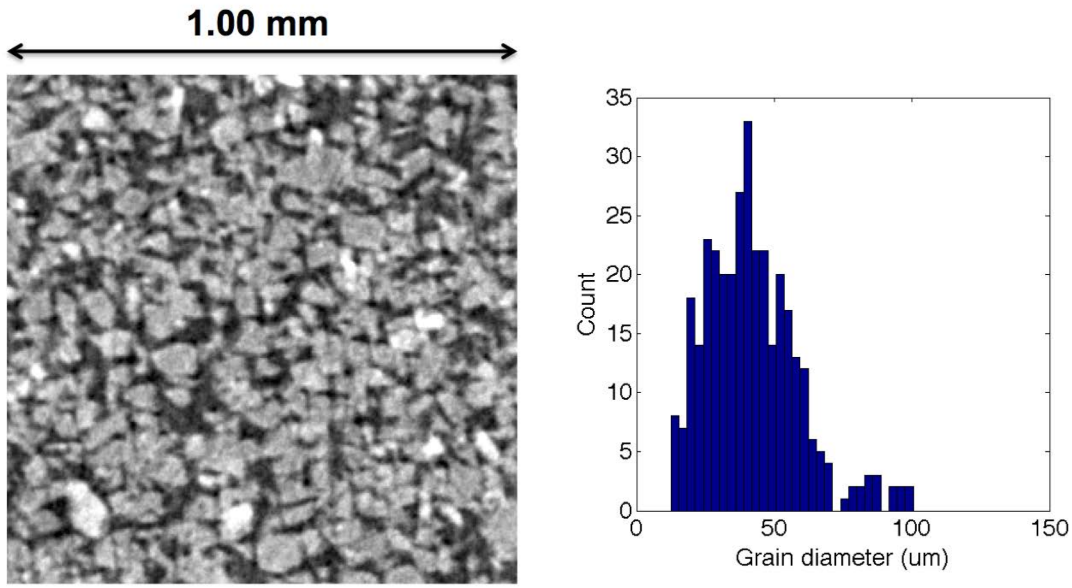

Figure 8.3 Left: micro-CT image (resolution: 3.50 µm) of Gulf of Mexico sand, which is the dissociated sediment sample from the GOM2 project (Well GC 955 H005, lithofacies 2, depth 415-450m below sea floor) provided by Steve Phillip. Right: grain size distribution based on the CT image.

We have built up a small sample vessel suitable for imaging the GOM2 fine sand as planned in the previous quarterly report. The diameter of the sample vessel is 4.7 mm and its distance to the X-ray gun is 34 mm, such that the resolution is 3.50 µm. We started with a trial experiment forming xenon hydrate in the GOM2 sand sample. The experimental procedure follows.

We mix oven-dry GOM2 sand with 4.37 wt% KI brine to achieve an initial water saturation of 50%. The micro-CT image before xenon gas injection did not show clear evidence of free water in the pore space yet (Fig. 8.4 left). Likely, some of the water remained in the small pores in between silts (grain size < 75 µm) and clays, with low resolution for proper segmentation. The experimental temperature is the room temperature of 23.0 °C and the equilibrium pressure is 1.61 MPa at 23.0 °C with a salinity of 4.37 wt% KI. The initial gas pressure is 3.21 MPa to allow xenon hydrate formation. The gas pressure stays at 3.21 MPa after 2 days of xenon gas injection and the micro-CT image (Fig. 8. 4 right) does not show any xenon hydrate within the pore space. This is likely due to no free water in the pore space. The increase of overall grayscale number in the CT image after 2 days is a result of xenon gas strongly attenuating X-rays.

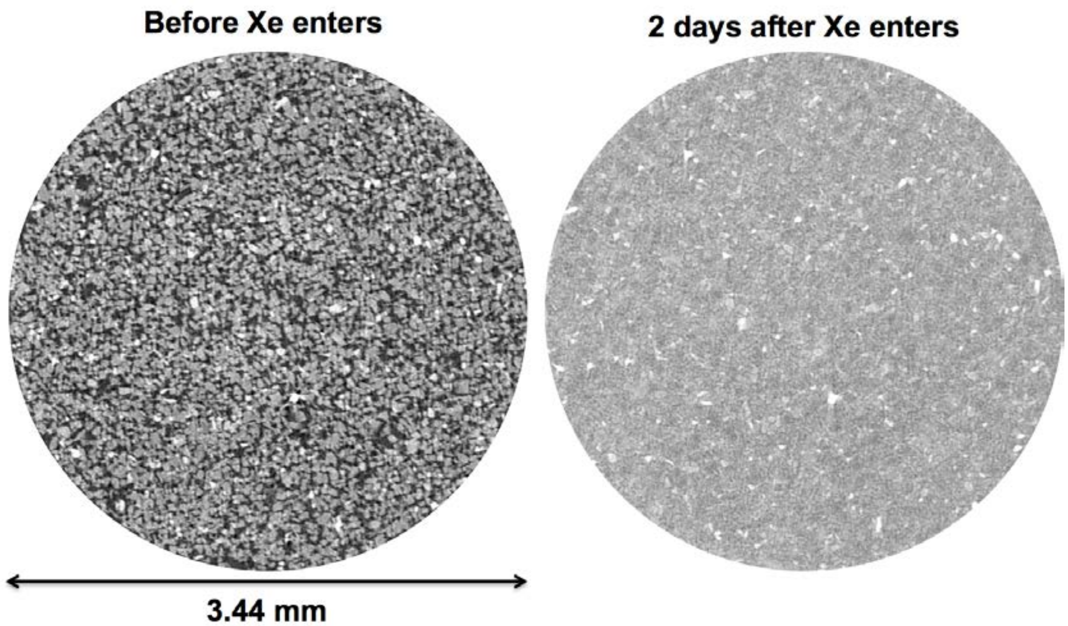

Figure 8.4 Left: micro-CT image of GOM2 sand before xenon gas injection at a resolution of 3.50 µm. Right: micro-CT image at the same location 2 days after xenon injection.

[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

We are currently dissociating methane hydrate in the coarse sand by step-wisely decreasing the gas pressure. We will report these results in the next quarterly report. These results can provide insights for production tests in the GOM2 sand, which is finer than the coarse sand by one order of magnitude. The next step is to dissociate hydrate from GOM2 sands.

[Link to actions for next Quarter, Task 8]

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

Subtask 9.1 3D Imaging of methane hydrate sandpacks
Planned Finish: 1/17/19
Actual Finish: In Progress

We started and finished a methane hydrate formation and dissociation test in silica glass beads, under relevant pressure and temperature conditions of hydrate reservoirs in the Gulf of Mexico. We used 3.5 wt% NaCl pore fluid to simulate the seawater environment. Fig. 9.1 show the pressure and temperature trajectories over time, in relationship to the methane hydrate stability phase boundary. The liquid water and methane system was step-wise cooled to enter the hydrate stability zone. Methane hydrate formed with 11 K of subcooling.

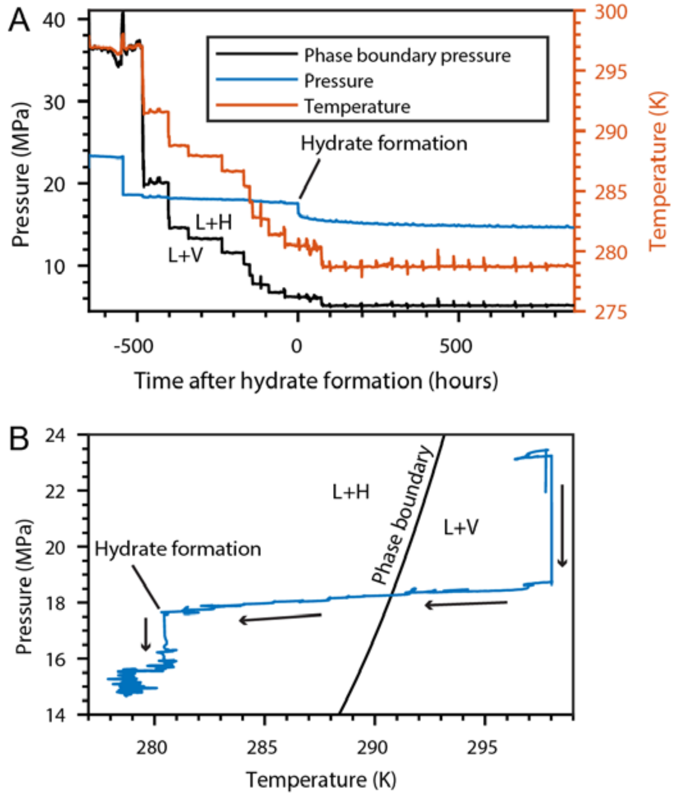

Figure 9.1. Pressure and temperature trajectories of a methane hydrate formation experiment. (A) Pressure and temperature over time are depicted by the blue and the orange lines, respectively. The black line represents the phase boundary pressure at the given temperature, with 3.5 wt% NaCl in the pore fluid, resembling seawater salinity. Above the boundary, liquid water (L) and methane hydrate are stable. Below, liquid water (L) and vapor methane (V) are stable. After the initial sample loading, the sample entered the hydrate stability zone (where the blue line is below the black line) by lowering the temperature. The duration between -400 hours to 0 hours represents the induction time. In a constant-volume reaction chamber, the hydrate formation is characterized by the sudden pressure decrease at 0 hour. (B) Pressure and temperature evolutions are plotted in respect to the phase boundary. Hydrate formed with 11 K subcooling.

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 deployed a Raman spectrometer to conduct 2D mapping over an area (2 mm by 2 mm) of methane-hydrate-bearing glass beads (210-290 μm in diameter). Each Raman data acquisition location is 25 μm apart in both X and Y directions. Thus, we acquired 6561 (81 by 81) acquisition points in each map. In Fig. 9.2, we represent the spatial and temporal distributions of hydrate structure type, derived from the Raman spectrum at each acquisition point.

Structure-I (sI) hydrate is the thermodynamically stable hydrate at the experimental condition. In Fig. 9.2, the sI hydrate is characterized by the slope of 3, as its quantity of large cages is three times the quantity of small cages. However, sI hydrate did not form immediately after the initial hydrate formation (1.93 hours). Over time, the hydrates gradually converted to sI hydrate, indicate by Raman peak areas along the slope of 3.48 (Fig. 9.2).

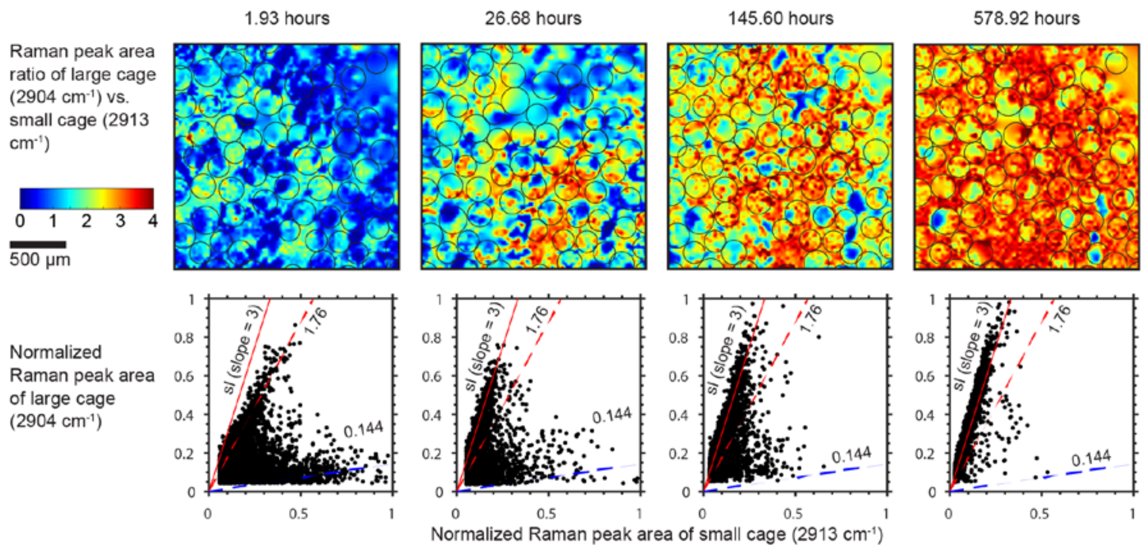

Figure 9.2. Pseudocolor maps and plots derived from Raman mapping data at three representative timestamps (1.93 hours, 26.68 hours, 145.60 hours, and 578.92 hours). A total of 6561 Raman measurement points (81 by 81 array) were acquired in each map, over an area of 2 mm by 2 mm at 25 µm step spacing. **Top:** The Raman peak area ratios of large cages (2914 cm^{-1}) to small cages (2904 cm^{-1}) imply hydrate structure types. A ratio of 3.0 indicates structure-I (sI) hydrate (yellow color). Black circles outline the positions of the glass beads (porous medium). **Bottom:** Raman peak areas of large vs. small cages of 6561 Raman measurements (less bad or meaningless data points). The slope of 3 indicates sI hydrate.

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 3 post-doctoral scientists.

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

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 Y2Q3 Quarterly
- Update the HP3 Website
- Steve Phillips will present an update of the project to the DOE at the Aug '18 meeting.

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: 1/17/19
Actual Finish: In Progress

- We will continue to perform brine and methane co-injection in the presence of hydrate in sandstone cores to obtain full drainage relative permeability curves for brine and methane in the presence of different hydrate saturations.

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 1/1/19

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 form hydrates using the formation method used in Task 2.0 to obtain hydrate saturations > 40% and then depressurize while observing pressure rebound behavior. This will allow us to observe the influence of hydrate saturation and formation method on the form of pressure rebounds.

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

- We will continue depressurize pressure core samples recovered during the UT-GOM2-1 Expedition. We will slowly depressurize these samples while monitoring pressure rebounds between steps during dissociation. This approach will allow us to observe the influence of lithology and hydrate saturation on pressure recovery behavior during dissociation. We will look at the influence of lithofacies (sandy silt vs. clayey silt) and hydrate saturation (5 to 93%) on pressure rebound behavior.

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

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

- We will prepare the GOM2 sample by first fully saturating with brine and then decreasing water saturation by gravity drainage. This can ensure free water in the pore space to start hydrate formation.
- We will use a lighter noble gas, krypton, to form hydrate in the GOM2 sand sample, such that the gas phase will not look too bright in the CT image.

- We will develop a new cooling assembly for the small sample vessel such that we can also form methane hydrate in the GOM2 sand sample.

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

- We will finish and analyze our current methane hydrate dissociation experiment in the coarse sand.
- We will also dissociate krypton hydrate and methane hydrate in the GOM2 sand sample once the hydrate formation steps are finished.

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

Subtask 9.1 3D Imaging of methane hydrate sandpacks
Planned Finish: 1/17/19
Actual Finish: In Progress

- We will synthesize and dissociate methane hydrates in two types of porous media packed in a chamber. Half of the chamber is packed with natural depressurized silty sediments from the GOM^2 project, and the other half is packed with clay-free sediments. We will monitor the differences in methane hydrate formation and dissociation in those two types of porous media.

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

- Due to capillarity, the gas pressure of vapor methane may be elevated above the ambient pressure. We will attempt to determine the in situ pressure of vapor methane by Raman spectroscopy. We will obtain a calibration curve between the Raman shift and the pressure. This calibration curve will help us determine the in situ pore pressure during hydrate formation and dissociation processes.

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

Xiongyu Chen, 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

Xiongyu Chen, 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

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.

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), Relative permeability of hydrate-bearing sediment, poster presented at Gordon Research Conference on Natural Gas Hydrate Systems, Feb. 25-Mar. 2, 2018, Galveston, TX.

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
- 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)

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): We had significant challenges developing consistent pressure drops in our sections in our relative permeability experiments using sand packs. We ultimately changed from performing these experiments on sand-packs to performing these experiments on Boise sandstone core. We are now making successful relative permeability measurements on the sandstone core. We may return to examining relative permeability in sand packs after completion of analysis of relative permeability on the sandstone core.
- Microscale Imaging (Task 8): It has been challenging to develop sufficient contrast to image gas, methane hydrate, and brine. For this reason, we have changed brines, decreased the

sample diameter and increased the imaging resolution. We will be using potassium iodide (KI) salts for the ensuing experiments and extend experiments to 1/8 in diameter.

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

At this time we do not anticipate any significant remaining budget at the end of the current budget period, 9/30/19.

5. BUDGETARY INFORMATION:

The Cost Summary is located 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		07/01/16-09/30/18	
	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		
Non-Federal Share	$ 19,857	$ 210,735	$ 7,140	$ 217,875	$ 32,567	$ 250,442		
Total Incurred Cost	$ 127,073	$ 605,928	$ 161,898	$ 767,826	$ 196,076	$ 963,902		
Variance								
Federal Share	$ (2,032)	$ (238,972)	$ 65,022	$ (173,950)	$ 34,595	$ (139,355)		
Non-Federal Share	$ 12,515	$ 11,542	$ (12,229)	$ (687)	$ 25,225	$ 24,538		
Total Variance	$ 10,483	$ (227,430)	$ 52,793	$ (174,637)	$ 59,820	$ (114,817)		

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								
Non-Federal Share								
Total Incurred Cost								
Variance								
Federal Share								
Non-Federal Share								
Total Variance								

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