NATIONAL ENERGY TECHNOLOGY LABORATORY

OIL & GAS

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Quarterly Research Performance Progress Report (Period Ending 6/30/2017)

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 first year of the first budget period. The majority of the progress made was purchasing parts to build the laboratory equipment and beginning to test that equipment.

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 will first demonstrate our ability to systematically manufacture sand-pack hydrate samples at a range of hydrate saturations. We will then 1) measure the permeability of the hydrate-saturated sand pack to flow of a single phase (water or gas), 2) depressurize the hydrate-saturated sand packs and observe the kinetic (time-dependent) behavior. Simultaneously we will build a micro-CT pressure container and a micro-Raman Spectroscopy chamber to image the pore-scale habit, phases, and pore fluid chemistry of our sand-pack hydrate samples. We will then make these 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)	11/22/2016	Presentation	Complete
Milestone 1.B: Achieve hydrate formation in sand-pack	6/27/2017 (Y1Q3)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 2.1)	In progress
Milestone 1.C: Controlled and measured hydrate saturation using different methods	3/27/2018 (Y2Q2)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 2.1)	
3 Milestone 1.D: Achieved depressurization and demonstrated mass balance	3/27/2018 (Y2Q2)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 3.1)	
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
Milestone 1.F: Achieved Hydrate formation and measurements in Micro-CT consolidation device	3/27/2018 (Y2Q2)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 4.1)	In progress
Milestone 1.G: Built and integrated high-pressure gas mixing chamber	3/27/2018 (Y2Q2)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 5.1)	In progress
Milestone 1.H: Micro-Raman analysis of synthetic complex methane hydrate	3/28/2018 (Y2Q2)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 5.1)	In progress
Milestone 2.A - Measurement of relative permeability in sand-pack cores.	1/17/2019 (Y3Q2)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 6.1)	
Milestone 2.B - Measurement of relative permeability in intact pressure cores.	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.	9/30/2019 (Y3Q4)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 7.1)	
Milestone 2.D - Achieved gas production from GOM^2 samples monitored by micro-CT.	9/30/2019 (Y3Q4)		Documentation of milestone achievement within required project reporting / deliverables Report (Deliverable 8.1)	
Milestone 2.E - Building a chamber to prepare natural samples for 2D-3D micro-Raman analysis;	1/17/2019 (Y3Q2)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 9.1)	
Milestone 2.F - 2D micro-Raman analysis of natural methane hydrate samples at depressurization;	9/30/2019 (Y3Q4)		Documentation of milestone achievement within required project reporting / deliverables (Deliverable 9.1)	

B. What was accomplished under these goals?

CURRENT- BUDGET PERIOD 1

Task 1.0 Project Management and Planning

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

- The second Quarterly Report was submitted on June 13, 2017
- Submitted a revised Data Management Plan (DMP)

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: In progress

- During this quarter we finished our purchasing requests for equipment and began assembling equipment as it arrived or was made available. To begin the process of forming hydrate, we have assembled two pumps and an existing core holder to allow us to form hydrate while waiting for new equipment to arrive. The pumps and core holder have been connected and leak-tested.

Subtask 2.2 Steady-State Permeability of Gas and Water of Sand-Pack Hydrate Samples
Planned Finish: 3/27/18
Actual Finish: Not Started

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

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

- We submitted a publication covering the freshwater dissociation experiment from the first quarter. The manuscript "Dissociation of laboratory-synthesized methane hydrate in coarse-grained sediments by slow depressurization":
- We worked on planning of additional hydrate formation for depressurization experiments and assembly of equipment in coordination with the efforts in Task 2.0.

Subtask 3.2 Depressurization Tests with CAT scan
Planned Finish: 03/27/18
Actual Finish: Not Started

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

During this quarter we have completed Milestone 1.E: “Build and test micro-consolidation device” (See separate Milestone report). Figure 4.1 shows the micro-consolidation device including the temperature controller. Formation and dissociation of methane-hydrates are observed by performing the experiments in the X-ray micro computed tomography (micro-CT) apparatus.

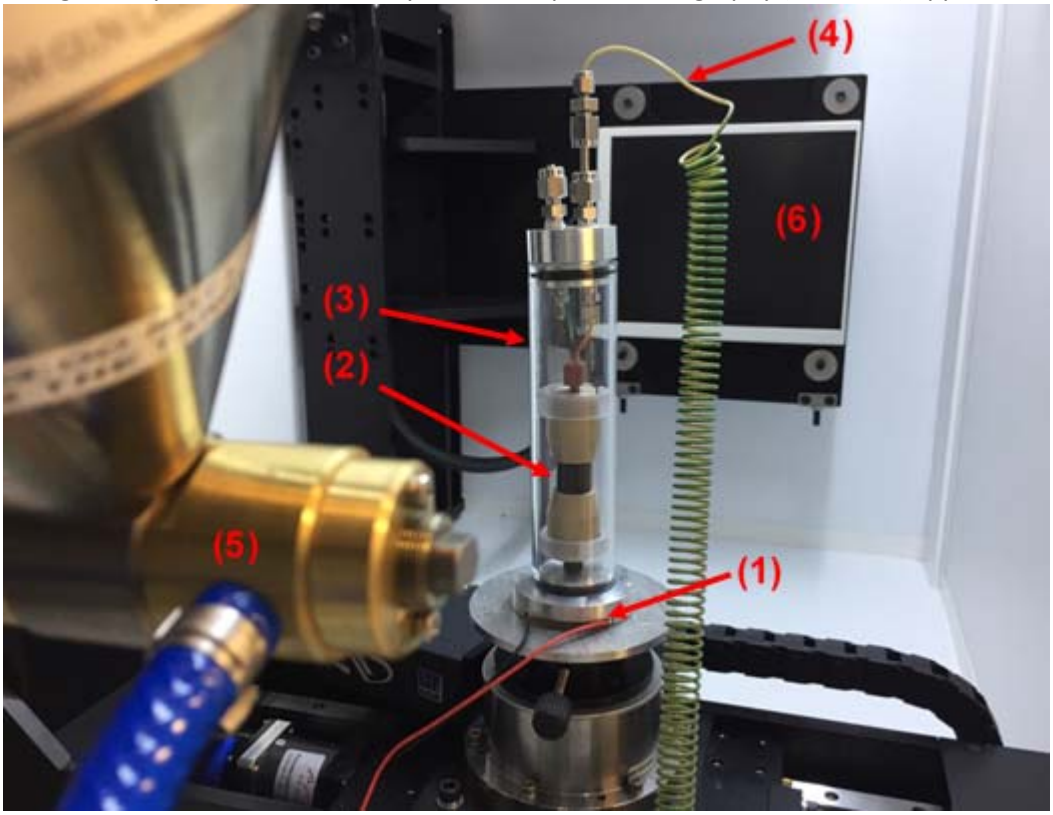

Figure 4.1. Micro-consolidation device. The experimental setup includes: temperature reading, recording and control system, whose main part is represented by the Peltier cell (1); (2) The micro-consolidation device cell, which is made of PEEK; (3) The cooling jacket; and (4) Pressure control through a high-pressure gas accumulator. 5 and 6 are the source and detector of the micro-CT apparatus, respectively.

To form and dissociate methane-hydrates a Peltier cell (Figure 4.1, detail 1) varies the temperature of the micro-consolidation cell at desired rates. A MOSFET H-bridge circuit powers the Peltier cell and a microcontroller board (Arduino UNO) integrates a proportional integral derivative (PID) controller and a couple of temperature sensors controlling the MOSFET H-bridge circuit. The Arduino UNO permits also to record continuously (i.e., sampling rate ~2Hz) the temperature and pressure of the micro-consolidation cell. Data are directly stored in a micro secure-digital (SD) card. Figure 4.2 shows the schematic wiring connecting from the Arduino UNO to a MOSFET H-bridge, a 5V battery, a Peltier cell, a 12 V auto battery, two thermistor sensors, and the micro-SD breakout.

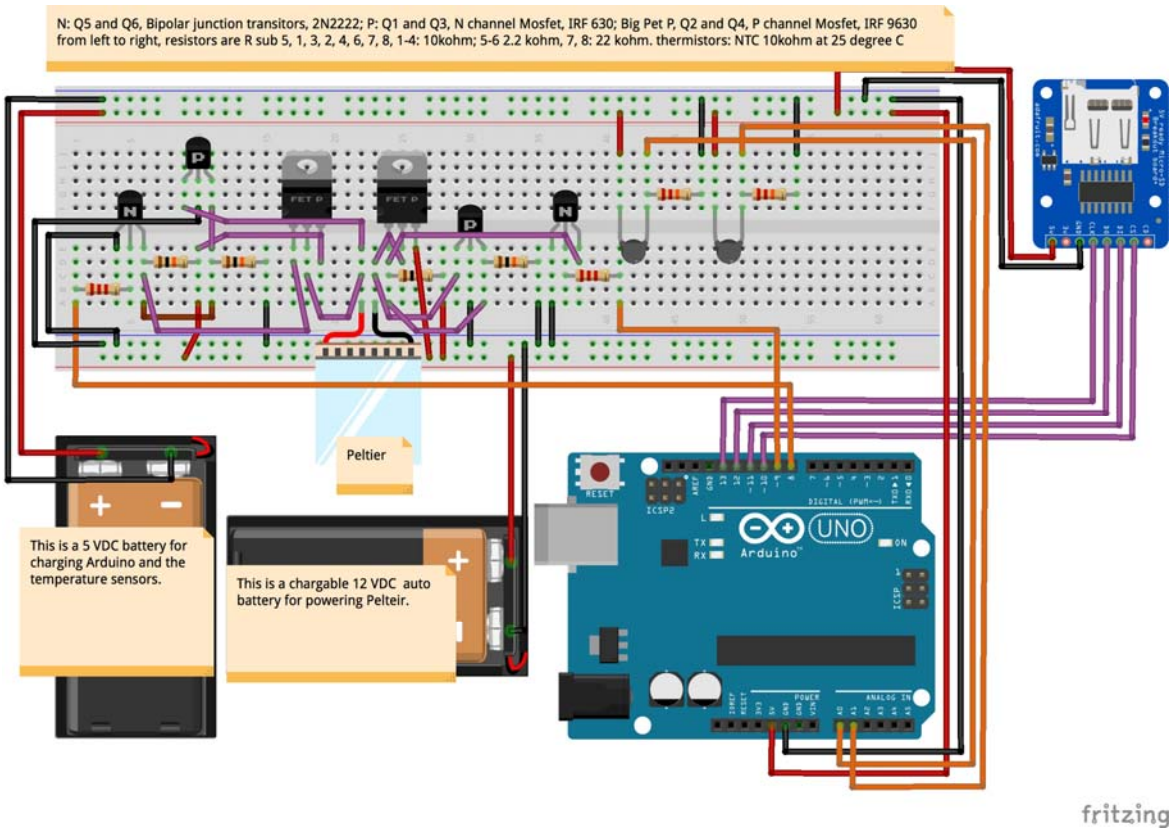

Figure 4.2. Schematic wiring of the control and recording system based on Arduino UNO board. From left to right: MOSFET H-bridge, Peltier cell, thermistors, and micro-SD breakout (snapshot from open source software fritzing,org).

The milestone report in Appendix A documents additional details.

Subtask 4.2 Micro-Scale CT Observations and Analysis
Planned Finish: 03/27/18
Actual Finish: In Progress

During this quarter we have analyzed xenon hydrate experiments, identified pore habit and measured permeability through lattice Boltzmann numerical simulations. We are also running methane hydrate experiments and are developing methods to enhance contrast between CH_4 hydrate and brine for segmentation.

Figure 4.3a shows examples of CT slices along the micro-consolidation device. The figures show hydrate growth and habit evolution under excess gas conditions at two depths from the lower endcap. Xenon hydrate (bright) is present in different pore habits and evolves with time. At slice A, pore habit starts as grain-coating and evolves towards progressively larger crystals at the mineral-gas interface. Section B shows evolution of hydrate from grain-coating to pore-filling. The evolution proceeds in excess gas conditions and -we hypothesize- as a result of Ostwald ripening. Figure 4.3c summarizes the evolution of hydrate with time and Figure 4.3d the expected reduction in permeability assuming a Corey-type relationship.

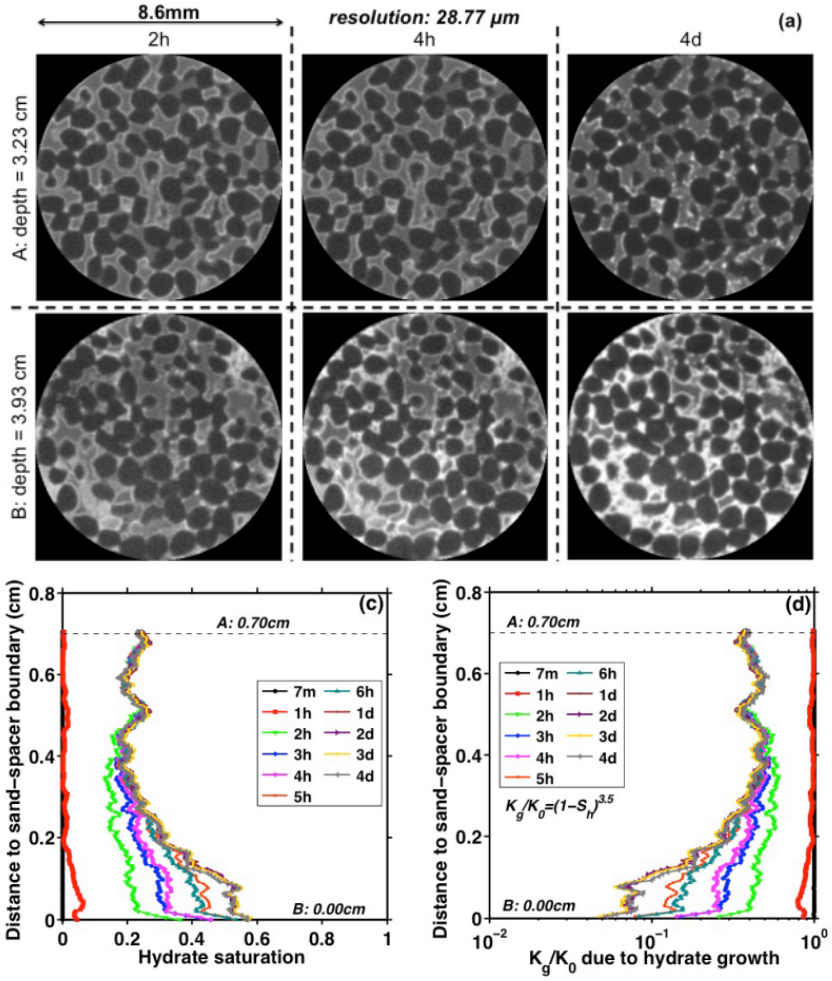

Figure 4.3. Xenon hydrate growth in sandpack: Ostwald Ripening makes hydrate pore habit change from grain-coating to pore-filling, and make hydrate saturation and reduced permeability heterogeneous in space. (a) CT slices at two locations (A&B) vs. time; (c) hydrate saturation profiles and (d) reduced permeability profiles.

In preparation for experimental measurement of hydrate-bearing sand permeability, we have performed numerical estimations based on tomographic images at the pore scale. These images permit mapping the location of various solid and fluid phases in actual hydrate-bearing sand. In collaboration with Dr. Prodanovic (UT Austin – no cost to this project) we are utilizing tomographic images to compute sediment permeability using lattice Boltzmann simulations. Figure 4.4 shows two examples of calculation of permeability in a dry sand pack and in a hydrate-bearing sand. The original tomographic images undergo segmentation to identify grains, hydrate, water, and gas. These images are then used to generate a domain for fluid flow simulation. Preliminary results show that the heterogeneous distribution of hydrate imposes large variations in reduced permeability ranging from 40% to 2% of the absolute permeability for hydrate saturation ranging from 10% to 60% respectively.

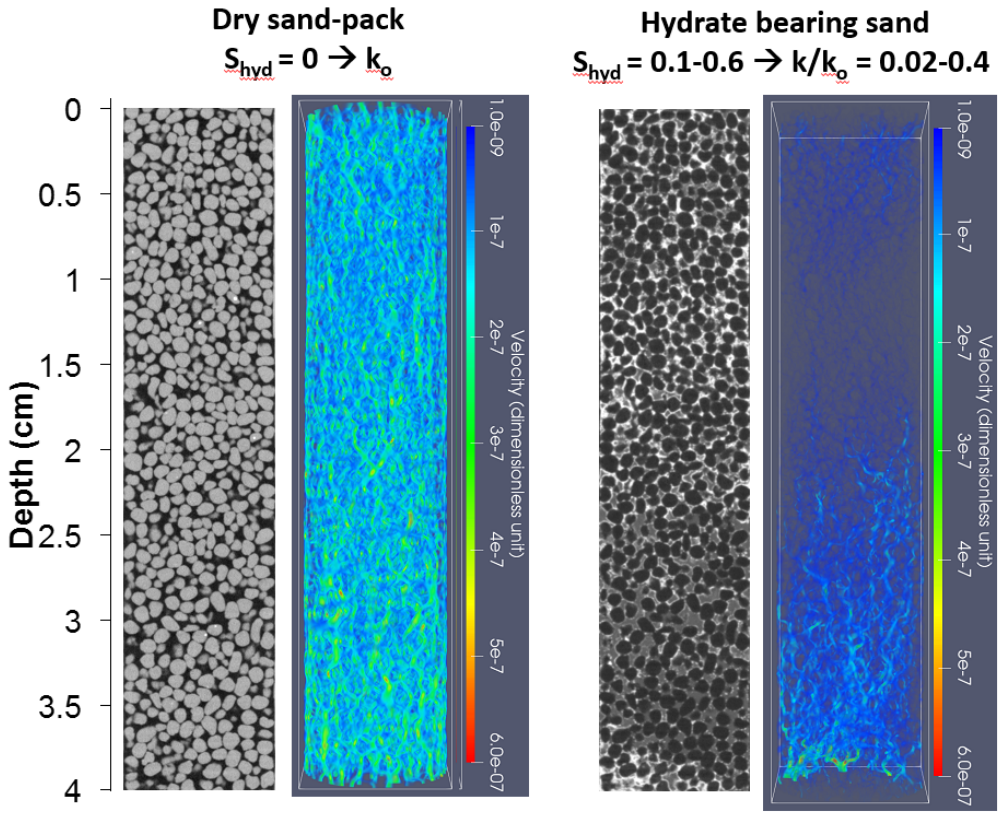

Figure 4.4. Permeability calculation in dry sand pack and in hydrate-bearing sediment. Images show a vertical slice of the 3D domain together with a snapshot of flow velocity field from lattice Boltzmann simulations. The presence of hydrate lowers permeability up to 2 orders of magnitude.

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: Complete

We have designed and built a functional micro-Raman compatible pressure vessel, with a pressure capacity of 4000 psi and a temperature control down to 0 °C. We logged the pressure, vessel temperature, and room temperature with a customized LabView program. The vessel holds ~0.65 cm^3 of porous media. We use micro-Raman spectroscopy to document the methane hydrate in the porous media through the sapphire window.

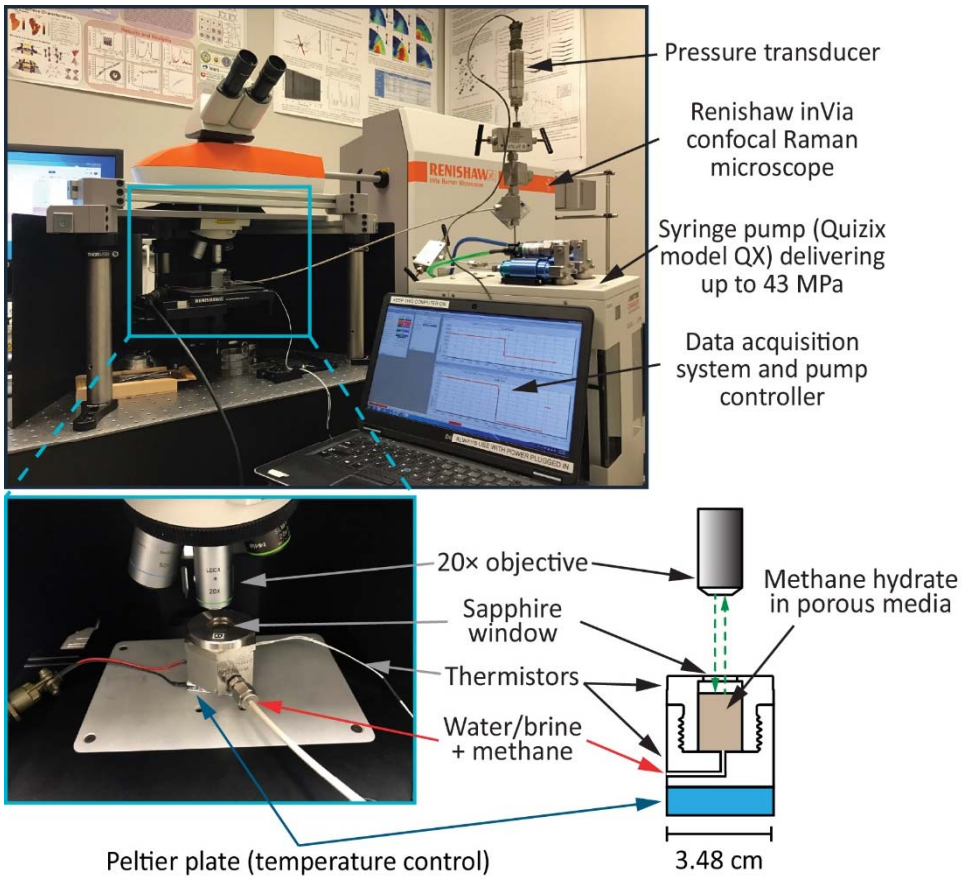

Figure 5.1. Fully functional high-pressure cell under micro-Raman spectroscopy at UT-Austin. The Raman cell is placed under the Raman microscope for spectral examination. We have built a LabView Program in a portable computer to monitor the pressure and temperature of the sample chamber.

Subtask 5.2 Micro-scale petrochemistry
Planned Finish: 03/31/18
Actual Finish: In progress
During this quarter, we synthesized methane hydrate in porous medium (glass beads) in the “static” hydrate vessel that we designed and built, using “excess water” technique. The glass beads were initially filled with methane vapor. Water was supplied to compress the methane vapor and elevate the pressure to hydrate stability zone (15 MPa and 3 °C). We monitored the hydrate formation with optical imaging and micro-Raman spectroscopy. In addition to hydrate formation, we dissociated the methane hydrate by slowly decreasing the pressure.

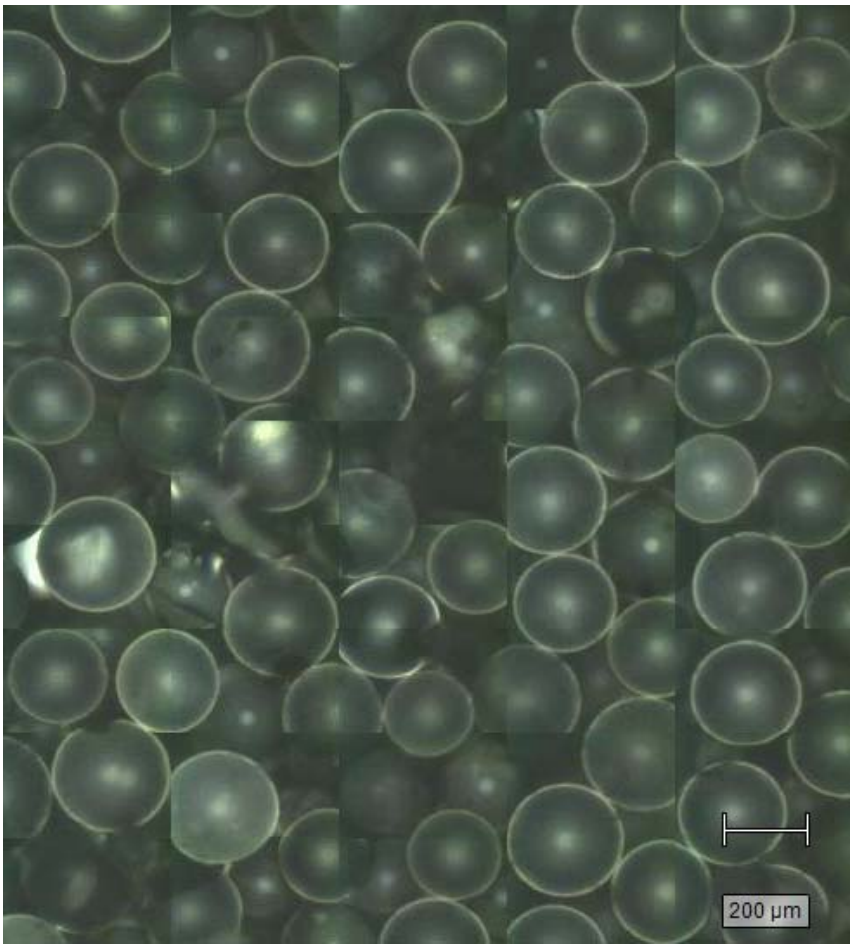

Figure 5.2. Porous media (glass beads) of 210 –293 µm in diameter, prior to methane hydrate formation. The pore size ranges from ~30 µm to ~300 µm. As a starter, we use glass beads as a simplified version of natural quartz sand. We will use natural quartz sands and natural sediments from the Gulf of Mexico to compare our results. The horizontal and vertical lines are artifacts due to image stitching.

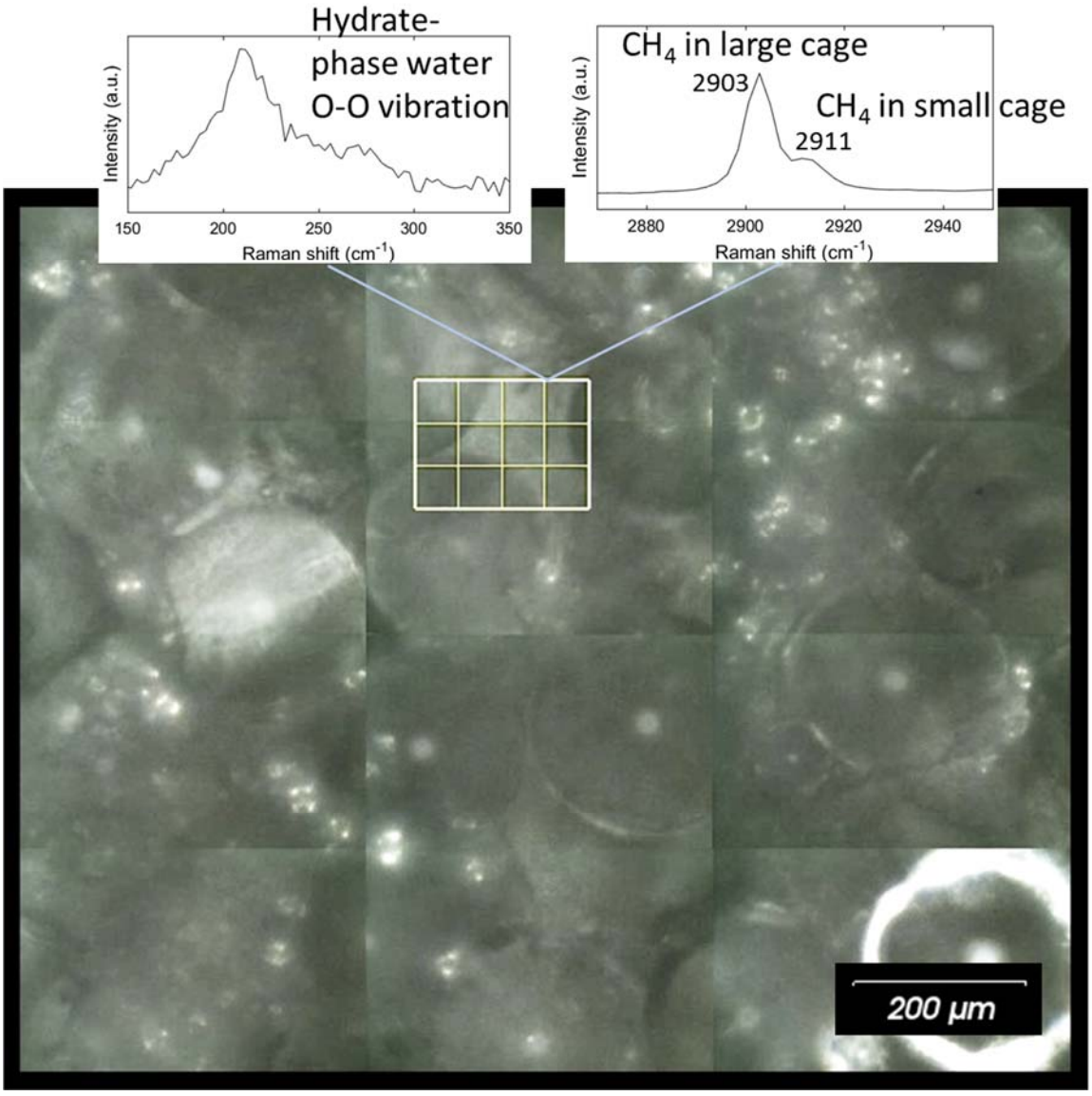

Figure 5.3. Methane hydrate formed in porous media (glass beads). The horizontal and vertical lines are artifacts due to image stitching. Methane hydrates have 2 ranges of characteristic Raman peaks: (1) the oxygen-oxygen translational stretching mode of water molecules in hydrate lattice between 200^{-1} and 300 cm^{-1} and (2) the carbon-hydrogen symmetrical stretching mode of methane molecules in hydrate at 2903 cm^{-1} and 2911 cm^{-1}. The peak intensity ratio of large cage to small cage is 2 to 1, inferring structure I hydrate.

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

We dissociated methane hydrates at 15 MPa and ~17.5 °C in freshwater condition in porous media (glass beads). We collected optical images and Raman mapping measurements on the vapor methane and dissolved methane concentrations. Figure 5.4 shows a snapshot immediately after hydrate dissociation by depressurization. Most of the pore volume is occupied by methane vapor. Capillary force bounds the water between grains.

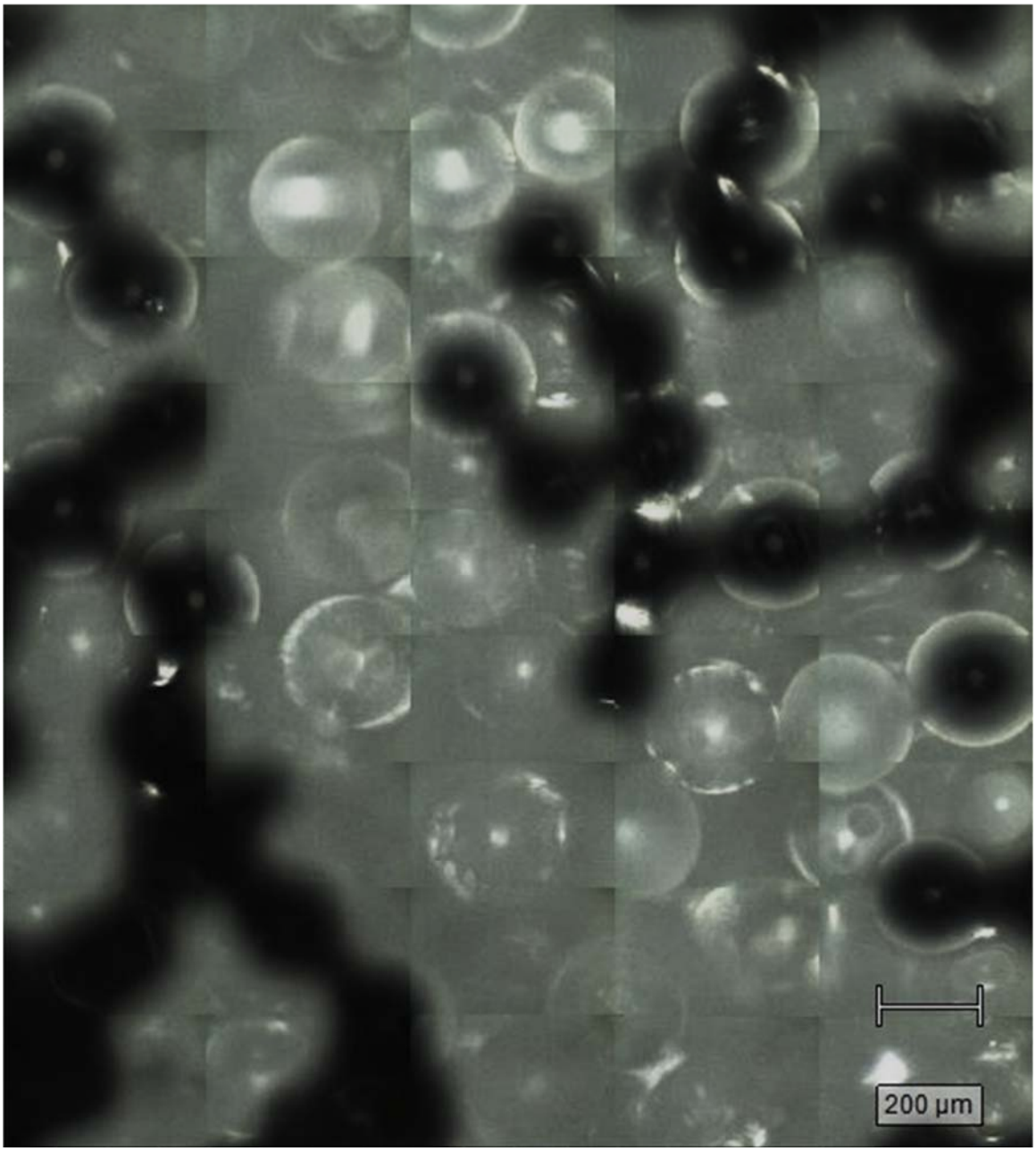

Figure 5.4. Optical image of the porous medium (glass beads) after hydrate dissociation. The bright regions are filled by methane vapor. The dark regions are filled by water. The horizontal and vertical lines are artifacts due to image stitching.

Decision Point: Budget Period 2 Continuation

Nothing to report this period.

FUTURE – BUDGET PERIOD 2

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: Not Started

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: Not Started

Subtask 7.2 Depressurization of intact pressure cores
Planned Finish: 9/30/19
Actual Finish: Not Started

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: Not Started

Subtask 8.2 Production Testing on GOM2 Samples Observed with Micro-CT
Planned Finish: 9/30/19
Actual Finish: Not Started

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: Not Started

Subtask 9.2 Micro-Raman Imaging of methane hydrate sandpacks
Planned Finish: 9/30/19
Actual Finish: Not Started

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

Nothing to Report

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.

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

a. Task 1.0 Project Management and Planning

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

- Continue working on external project website

b. 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: In progress

- Sand will be prepared in a moist state, mixed with kaolinite for better hydrate nucleation, and tamped into the core holder to a porosity of 35-40% and initial water saturation of 40%.
- Methane will be pumped in to a gas saturation of 60%. After doing this, the apparatus will be moved into the cold room and allowed to cool to 4°C.
- Methane consumption and pump pressure will be monitored to assess formation of hydrate. When the pressures and volumes stabilize, formation will be assumed to be complete. This method will yield hydrate saturation around 50%.

Subtask 2.2 Steady-State Permeability of Gas and Water of Sand-Pack Hydrate Samples
Planned Finish: 3/27/18
Actual Finish: Not Started

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

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

- Additional depressurization experiments in which we vary the magnitude of gas release at various stages of depressurization to test the pressure rebound due to salt diffusion to varying volumes of freshwater release.
- Additional depressurization experiments at hydrate saturation higher than we've previously accomplished (greater than 27%).

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

- We have scheduled time on the CT scanner in September to run at least one depressurization experiment.

d. 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: Complete

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

- Continue with methane hydrate growth and monitoring. Analysis will add computational fluid dynamic calculations to determine the influence of pore-habit and spatial variability on permeability of hydrate-bearing sand.

e. 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: Complete

Subtask 5.2 Micro-scale petrochemistry
Planned Finish: 03/21/18
Actual Finish: In progress

- We will use glass beads of smaller diameters (160–212 μm) to better simulate natural fine-sand gas hydrate reservoirs. We also plan to synthesize hydrates in the natural sediments recovered from the Green Canyon 955 site in the Gulf of Mexico by the Genesis of Methane Hydrate in the Gulf of Mexico project.
- To better simulate reservoir condition, we will synthesize and dissociate methane hydrate at the inferred reservoir condition at Green Canyon 955 (~24.5 MPa and ~19 °C).
- We will use “excess gas” method to synthesize methane hydrates

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

- In addition to monitoring dissolved methane diffusion kinetics, we will synthesize and dissociate methane hydrate using salt water at a range of salinities (3.5 wt% to 7 wt% NaCl) and observe the dynamic salt ion migrations in pore space, in respect to time and porous media.

2. PRODUCTS:

What has the project produced?

Research Performance Progress Report (Period ending 12/31/16)
Research Performance Progress Report (Period ending 3/31/17)

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.

Phillips, S.C., You, K., Flemings, P.B., Meyer, D.W., and Dong, T., in review. Dissociation of laboratory-synthesized methane hydrate in coarse-grained sediments by slow depressurization. Marine and Petroleum Geology

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

Nothing to Report.

c. Technologies or techniques

Nothing to Report.

d. Inventions, patent applications, and/or licenses

Nothing to Report.

e. Other products

Nothing to Report.

3. CHANGES/PROBLEMS:

This section highlights changes and problems encountered on the project.

a. Changes in approach and reasons for change

Nothing to Report.

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.

CURRENT - BUDGET PERIOD 1

Nothing to Report

FUTURE – BUDGET PERIOD 2

Nothing to Report

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		
Non-Federal Share	$ 10,800	$ 10,800	$ 10,800	$ 21,600	$ 10,800	$ 32,400		
Total Incurred Cost	$ 17,549	$ 17,549	$ 61,703	$ 79,252	$ 78,595	$ 157,847		
Variance								
Federal Share	$ (276,748)	$ (276,748)	$ (31,135)	$ (307,883)	$ (11,896)	$ (319,779)		
Non-Federal Share	$ (159,663)	$ (159,663)	$ 3,671	$ (155,993)	$ 3,671	$ (152,322)		
Total Variance	$ (436,411)	$ (436,411)	$ (27,465)	$ (463,876)	$ (8,226)	$ (472,101)		

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

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								

Appendix A.

Milestone Report
Milestone 1.E: Build and Test Micro-Consolidation Device

SUMMARY

This milestone report summarizes our achievement of building and testing the micro-consolidation device for forming and imaging gas hydrate in sediments. The following sections summarize the conception, construction and testing of the device. At the time being, we have successfully tested the device. The device is accounts with standalone data acquisition to record and control pressure and temperature remotely. This feature is useful for controlling the device inside the microCT cabinet. The PIs in charge of this task are D.N. Espinoza and N. Tisato. X. Chen executed design, followed device construction, and performed experiments. J. Luo assisted with automation and data acquisition.

1. Device Conception

Fig.1 shows the initial conception of the device and experimental workflow. The micro consolidation device consists of a hard-walled pressure vessel transparent to X-rays that permits applying a constant vertical effective stress to the sediment. The vessel is small enough to obtain high scanning magnification and observe hydrate pore habit. The vessel should account with permeable endcaps for fluid injection. The vessel should resist pressure and temperature typical of natural hydrate bearing sediments (500 to 3500 psi and 1 to 10°C).

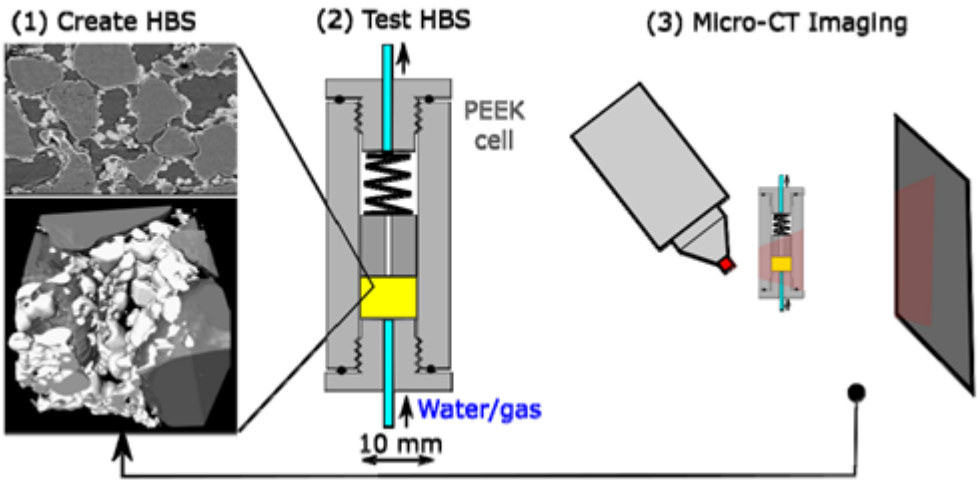

Figure1. Workflow for hydrate studies at the micro*s*cale (1) Example of pore scale imaging (Chaou achi et al., 2015). (2) Micro consolidation device that we will build to use with microCT imaging. (3) X-ray tomography schematics.

Figure 2 shows a diagram of the device for fluid flow, pressure and temperature control. The micro consolidation device connects to a small gas accumulator which is filled directly from the gas cylinder or from a pressure pump. A needle valve connects to the accumulator with the micro consolidation

device. A pressure transducer/gauge monitors pressure and a thermocouple monitors temperature. The micro consolidation device accounts with endcaps able to provide fluid injection and extraction. Inside the micro consolidation device the vessel accounts with permeable spacers to confine the sand pack. A stainless-steel spring provides effective stress to the sand pack through the movable spacers. An external heat sink provides temperature controlled to the entire device.

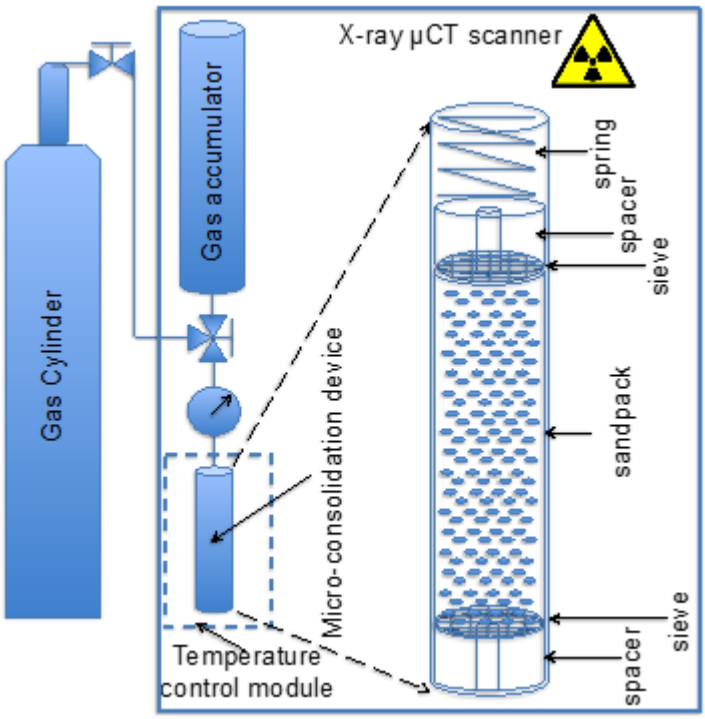

Figure 2. Schematic setup of micro-consolidation device.

2. Mechanical Construction

We have developed two versions of the micro-consolidation device. The first one is made of aluminum and constructed in our local machine shop. We utilized aluminum in order to combine high pressure resistance and thin walls in pressure vessels. All threaded fittings and valves are made of stainless steel. The second one is a shorter version made out of PEEK tubing and fittings. The temperature control consists on either a Peltier-cooled container or through a controlled-temperature bath and refrigerated coil tubes. Pressure control is achieved independently with a pressure pump ISCO 1000D.

Fig. 3 shows a photo the aluminum micro consolidation apparatus mounted in the X-ray micro-CT scanner. We have built 5 devices so far. The large aluminum vessel on the top is gas accumulator, and has (internal) dimensions of 2.0-cm-diameter and 8.6-cm-length. The small vessel in the bottom is the micro-consolidation device and has a (internal) dimensions of 0.86-cm-diameter and 7.2-cm-length. These two vessels are connected by stainless steel tubing, an analog gauge and a high-pressure stainless steel valve. The analog gauge is easily replaceable for a pressure transducer. However, the analog gauge is handy for storing in a controlled temperature container and it is extremely reliable over long experimental times (months). The radiography and CT slice of the micro-consolidation device show (from top to bottom): a compressed stainless steel spring (1.0 cm), a 1.1-cm-long PTFE spacer, a stainless steel sieve, a 4.0-cm-long sand pack, another stainless steel

sieve, and another 1.1-cm-long PTFE spacer. The spring applies an effective stress to the sand pack. The two sieves prevent sand going into the spacers. The system (as shown in Figure 3) is connected in closed mass conditions. Endcaps at the top and bottom permit the injection of fluids for measuring permeability.

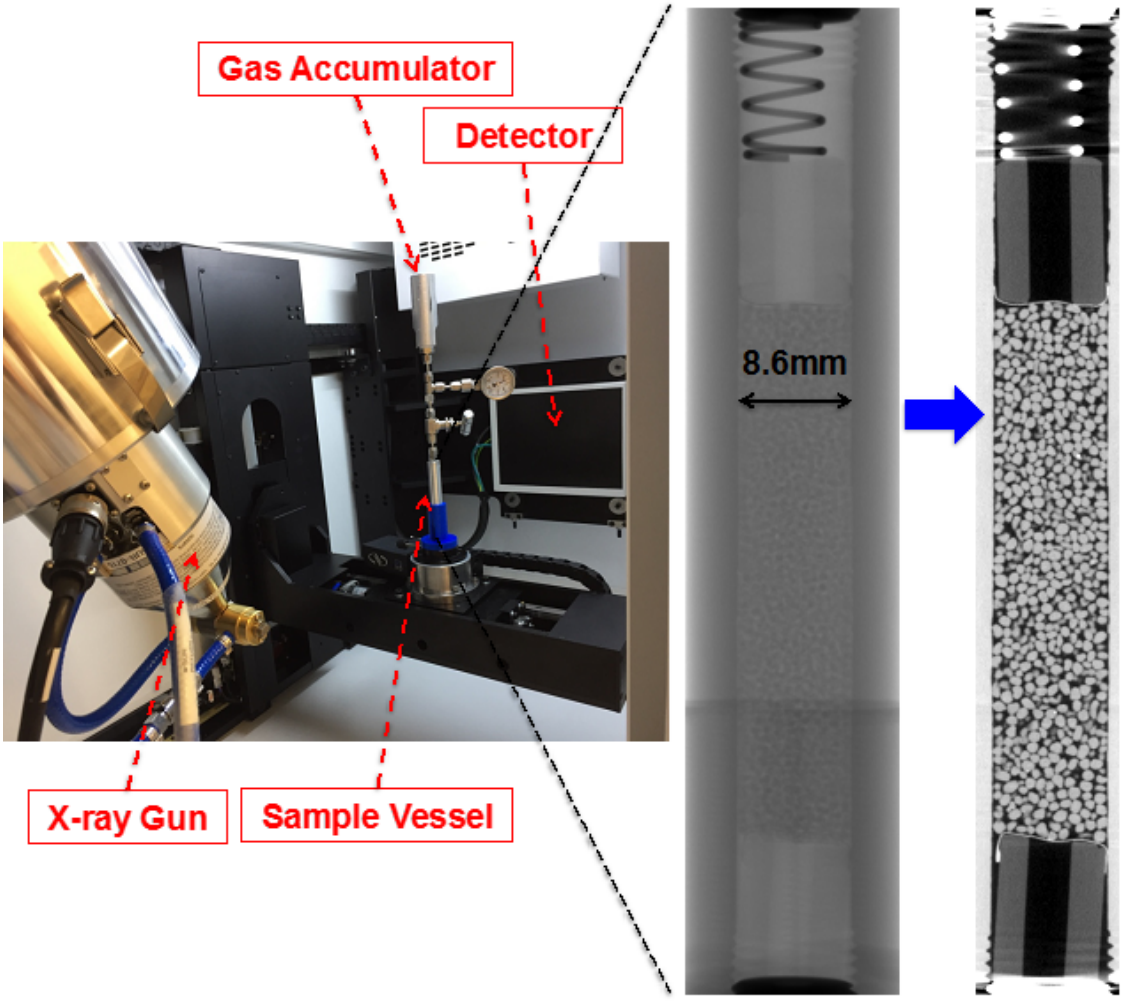

Figure 3. Long-term aluminum micro-consolidation device mounted in a micro-CT scanner with its radiography (center) and CT slice (right). The experimental apparatus consists of, from top to bottom, a large high-pressure vessel for storing gas, a pressure gauge, a needle valve and the micro-consolidation device. The micro-consolidation device is packed with a spring, two spacers and sand. Temperature isolation and module not shown in image.

Fig. 4 shows a photo the PEEK micro consolidation apparatus mounted in the X-ray micro-CT scanner. The device is similar to the aluminum version but it is shorter and more permeable to X-rays. In this picture the micro-consolidation device is capsuled in a cooling jacket controlled by a Peltier cell, and the high-pressure gas accumulator is connected to the device through the upper endcap. The flexible PEEK tubing connecting the device with the gas accumulator allows the device rotate smoothly by 360 degrees during CT scan. During experiment, the polycarbonate cooling jacket is filled with ethylene glycol. Two flexible polycarbonate rings attach to the ends of the PEEK tubing (the micro-consolidation device), which centralize the device. The cooling jacket is plugged with two aluminum end caps sealed by O-rings. On the bottom end cap, a Peltier cell is placed to cool down

or heat up the cooling jacket and the device. On the bottom of the Peltier cell, an active heat sink (not shown in picture) is attached to dissipate the heat of the Peltier hot side. The two thermistors are attached to the top and the bottom end caps to measure temperature. Foam insulation wraps (not shown) around the cooling jacket to prevent heat loss or heat gain from air.

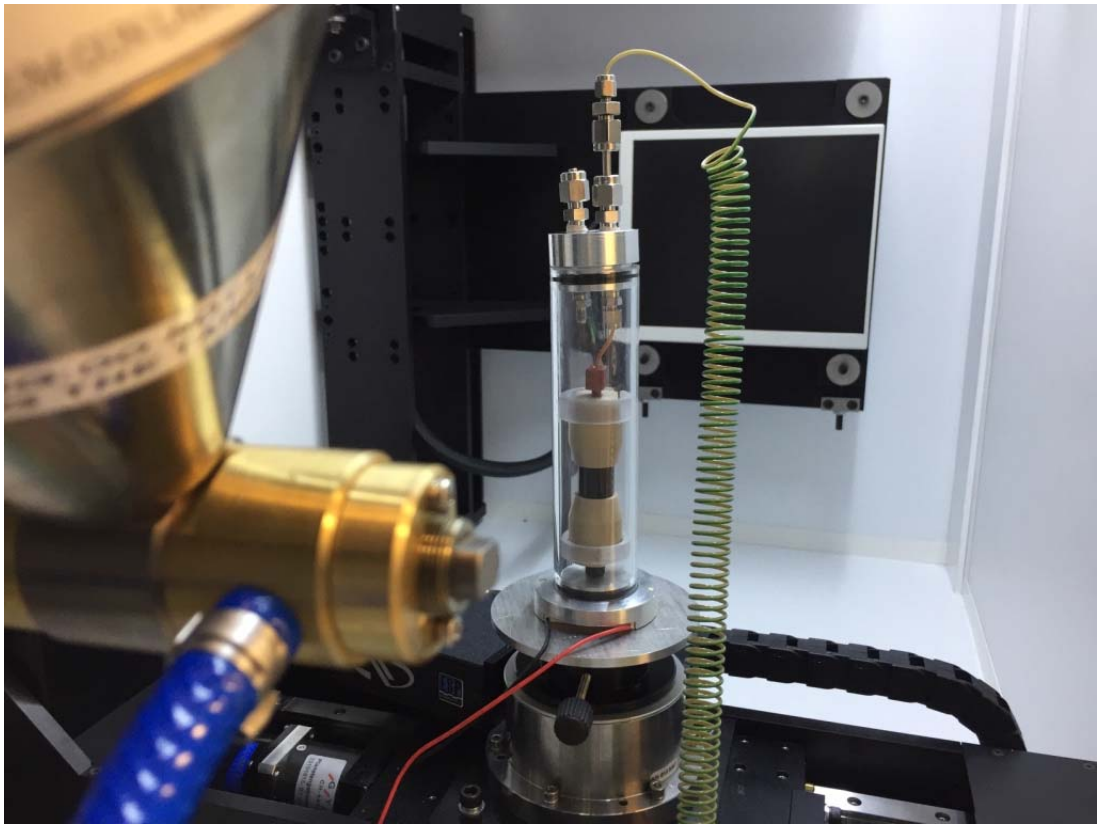

Figure 4. Peek micro-consolidation device. The experimental setup includes temperature reading and control system, the micro-consolidation device itself in the cooling jacket and pressure control through a high-pressure gas accumulator.

3. Automation and data acquisition

We have added an automatic data acquisition feature for temperature and pressure recording. A Peltier cell controlled with a MOSFET H-bridge circuit permits both increasing and decreasing the temperature of the device at desired rates and desired temperatures. Figure 5 shows the schematic wiring connecting from an Arduino processor to a MOSFET H-bridge, a 5V battery (for Arduino), a Peltier cell, a 12V (nominal) auto battery (for Peltier), two thermistor circuits, and a micro-SD breakout. Instead of directly connecting the Peltier cell to the 12V battery, the H-bridge is used to bridge between the battery and the Peltier cell. The H-bridge has two couple of gates that allow low-voltage signal inputs (such as 5V) to switch on, such that the Peltier cell is connected to the battery. The Arduino processor sends out 5V signals to either couple of the H-bridge gates (never turn on two couples together), such that, the current flow can be bi-directional to make Peltier cool down or heat up the micro-consolidation device. The temperature control system reads the temperature inputs from the two thermistor circuits (thermistors are attached to the micro-consolidation device) and substitute the average offset between targeted and measured temperatures into a PID algorithm

to determine the output percentage from the battery. Although Arduino only sends out 5V signals, a pulse-wave-modulation (PWM) algorithm is used to adjust the output percentage from 0% to 100%. Furthermore, the micro-SD card inside the breakout module records temperatures from the two thermistor circuits every 15 seconds. The whole process described in this paragraph is realized using the Arduino code in Appendix A.

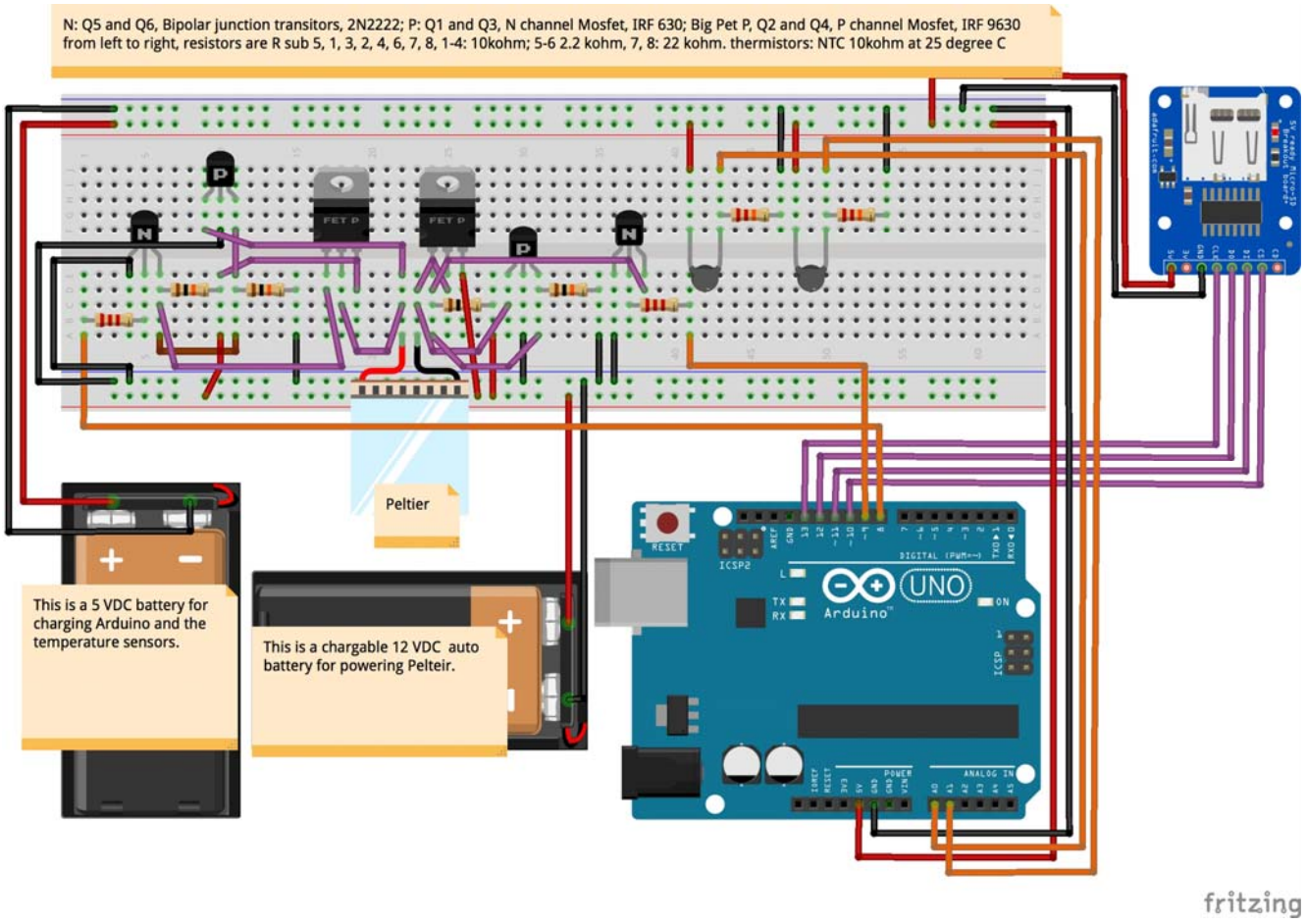

Figure 5. Schematic wiring from Arduino board to (from left to right) MOSFET H-bridge, Peltier cell, thermistors, and micro-SD breakout (snapshot from fritzing,org open source software).

4. Pressure Testing and Experimental Procedure

The aluminum micro-consolidation device has been successfully pressure tested with water, N_2, Xe, and CH_4 up to 1500 psi.

The procedure for pressure testing and hydrate formation is as follows:

(1) Connect the apparatus and leak test it at objective pressure, first with water and then with nitrogen gas.
(2) Pack the micro-consolidation device as shown in Fig. 2b and fill the accumulator with hydrate-forming gas.
(3) Fill the sand pack with water until desired water saturation.
(4) Set the micro-consolidation device to target temperature.

(5) Connect the micro-consolidation device with the gas accumulator to start the hydrate formation experiment.
(6) Record the temperature and pressure of the micro-consolidation device with time.
(7) Image the micro-consolidation device with the X-ray micro-CT at different resolutions to capture the hydrate nucleation and growth in the sand pack.
(8) Apply pressure gradient and measure permeability if required.

We have successfully also successfully tested the PEEK micro-consolidation device for temperature reading and control system and are running methane hydrate experiments.

5. Example of Hydrate Formation in Sand Pack

Fig. 6 shows an example of xenon hydrate growth in sand. Xenon hydrate is easily differentiated from sand grain and xenon gas in the CT slices because its high attenuation coefficient. The images highlight that (1) there is significant spatial heterogeneity in hydrate saturation, and (2) at low hydrate saturation (left), hydrate pore habit is mainly grain-coating while at high hydrate saturation (right), hydrate pore habit is a combination of grain-coating, pore-filling and grain-cementing.

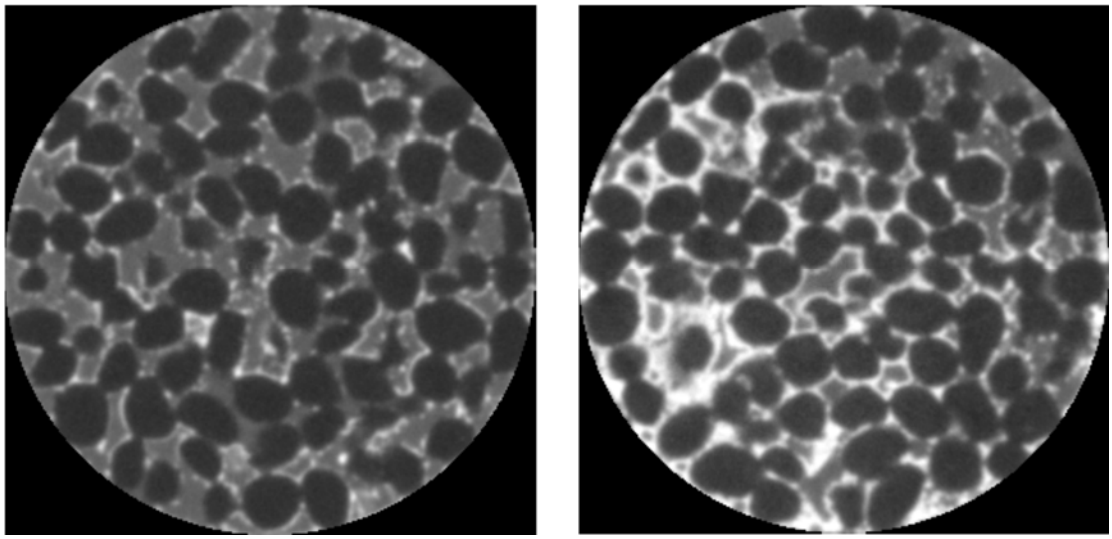

Figure 6. CT slices at two positions in sand after 4 days xenon hydrate growth (resolution: 28.77 μm). Xenon hydrate is white, sand grain is black and xenon gas is gray.

References

Chaouachi, M., Falenty, A., Sell, K., Enzmann, F., Kersten, M., Haberthür, D., and Kuhs, W. F., (2015),Microstructural evolution of gas hydrates in sedimentary matrices observed with synchrotron Xra y computed tomographic microscopy: Geochemistry, Geophysics, Geosystems, v. 16, no. 6, p. 17 11-1722, 10.1002/2015GC005811.

Circone, S., S. H. Kirby, and L. A. Stern (2005), Direct Measurement of Methane Hydrate Composition along the Hydrate Equilibrium Boundary, J. Phys. Chem. B, 109(19), 9468–9475, doi:10.1021/jp0504874.

Ohgaki, K., T. Sugahara, M. Suzuki, and H. Jindai (2000), Phase behavior of xenon hydrate system, Fluid Phase Equilibria, 175(1–2), 1–6, doi:10.1016/S0378-3812(00)00374-5.

Appendix A: Arduino code for temperature control feature

```
#include <SPI.h>
#include <SD.h>
#include <math.h>
File myFile;

// how many cylces data are logged, the period is approximately
// log_period/100 seconds
int log_period = 1500;

// Temp sensors def
double D1=1023; // Voltage at A0, for thermistor 1
double D2=1023; // Voltage at A1, for thermistor 2
double T1=23; // Temp measured by thermistor 1
double T2=23; // Temp measured by thermistor 2
// Initialization of T1 and T2 are room temp
double R1=20; // Resistance of thermistor 1
double R2=20; // Resistance of thermistor 2
double R3=19890; // Voltage divider for R1
double R4=19920; // Voltage divider for R2
double lnR1=20; // Natural log of R1
double lnR2=20; // Natural log of R2

// PID part def
double P_value=10; // PID parameters, proportional
double I_value=0; // PID parameters, derivative
double T_tar=4; // targeted temperature in C
double T_offset=T1-T_tar; // temp offset in C,
// The room temp is 23 C, assuming to cool down to 0C, Then initial
// T_offset is 23. To be safe, assuming the max T_offset is 30
double T_cumul; // cumulative T_offset along the time, for I_value

// Output part def
int led1 = 7;          // Connected to Z, Switch on NPN transistor
// and the P channel mosfet, switch device ground to positive Volt
int led2 = 6;          // connceted to u, Gate of N channel mosfet
// Switch device ground to ground.
// Warning, never turn on led1 and led2 at the same time. SHORTCUT

int led3 = 5;          // connected to A, Switch on NPN transistor
// and the P channel mosfet, switch device positive to positive Volt
int led4 = 4;          // connceted to H, Gate of N channel mosfet
// Switch device positive to ground.
// Warning, never turn on led3 and led4 at the same time. SHORTCUT

// led1 and led4 HIGH, led2 and led3 LOW, Device heating
```

```
// led2 and led3 HIGH, led1 and led4 LOW, Device cooling
// All low, device idle
// Warning, if led1 and led2 HIGH or led3 and led4 HIGH, SHORTCUT

double outpercent=T_offset*P_value; // This is the output percetage of the maxi
// -mum voltage of 13.02 V.
// This outpercent is [-100, 100]
// In my setup, positive means cooling, negative means heating

double maxvolt = 13.03; // the max voltage at battery
double x;
// This is the linear transformation from output percentage
// to the high duration
int high_duration;
// This is the duration of high
// After testing, this works when outpercent is between 11 and 100,
// But I think the output should be within [11, 80]%
// In most range, the relative error is 1% of expected voltage.

int maxtime = 10000; // This is the period in micro seconds, 0.01s

int count=0;

// int filtn=32;
void setup() {
  // put your setup code here, to run once:
  Serial.begin(9600);
  pinMode(led1, OUTPUT);
  pinMode(led2, OUTPUT);
  pinMode(led3, OUTPUT);
  pinMode(led4, OUTPUT);

  Serial.print("Initializing, ");
  pinMode(10,OUTPUT);
  if(!SD.begin(10)){
    Serial.println("failed");
    return;
  }
  Serial.println("done");

}

void loop() {
  // put your main code here, to run repeatedly:

  // Give the manual calibrated output to cool down or heat up
  // positive is cooling, negative is warming

  // default: set everything low, this is true when outpercent is
  // [-10.99, 10.99]
```

```
 if(outpercent < 11)
 {
   if(outpercent > -11)
   {
     digitalWrite(led1, LOW);
     digitalWrite(led2, LOW);
     digitalWrite(led3, LOW);
     digitalWrite(led4, LOW);
   }
 }

 // Cooling
 if(outpercent > 10.99) // output {11,100]
 {
   if(outpercent > 100) {
     outpercent=100;
   }

 digitalWrite(led1, LOW);
 digitalWrite(led2, HIGH);
 digitalWrite(led4, LOW);

 x = 784.83*(0.01*outpercent*maxvolt)-1117.04;
 high_duration = x;

 digitalWrite(led3, HIGH);
 delayMicroseconds(high_duration); // Approximately outpercent %
 // duty cycle @ 100 Hz
 digitalWrite(led3, LOW);
 delayMicroseconds(maxtime - high_duration);
 }

 // Heating
 if(outpercent < -10.99)
 {
   if(outpercent < -100) {
     outpercent=-100;
   }
 digitalWrite(led2, LOW);
 digitalWrite(led3, LOW);
 digitalWrite(led4, HIGH);

 x = 784.83*(0.01*(-outpercent)*maxvolt)-1117.04;
 high_duration = x;

 digitalWrite(led1, HIGH);
 delayMicroseconds(high_duration); // Approximately outpercent %
 // duty cycle @ 100 Hz
 digitalWrite(led1, LOW);
 delayMicroseconds(maxtime - high_duration);
```

```
}

// read T1 and T2, and use T1 to update output percent
//D1=0;
//D2=0;
//for(int n=1;n<=filtn;n++) {
//  D1=D1+analogRead(A0);
//  D2=D2+analogRead(A1);
//}
//D1=D1/filtn;
//D2=D2/filtn;

D1=analogRead(A0);
D2=analogRead(A1);

R1=R3*(1023-D1)/D1;
R2=R4*(1023-D2)/D2;
lnR1=log(R1);
lnR2=log(R2);

T1=319.72-36.471*lnR1+0.052763*lnR1*lnR1*lnR1;
T2=319.72-36.471*lnR2+0.052763*lnR2*lnR2*lnR2;

T_offset=T1-T_tar; // update temp offset
outpercent=T_offset*P_value; // update output percentage

if(outpercent > 100) {
   outpercent = 100;
  }

if(outpercent < -100) {
   outpercent = -100;
  }

// print out T1 and T2 every 10 seconds
count=count+1;
if(count > log_period){
  // print out the data
  Serial.print(T1); // T1
  Serial.print(" ");
  Serial.print(T2); // T2
  Serial.print(" ");
  Serial.print(outpercent); // outpercent
  Serial.print("\n");

 // Write data to micro-SD card
 myFile =SD.open("temp.txt",FILE_WRITE);
 myFile.print(T1);
 myFile.print(" ");
 myFile.print(T2);
```

```
    myFile.print(" ");
    myFile.print(outpercent);
    myFile.println("\n");

    // close the file:
    myFile.close();
    //Serial.println("done");
    count=0;
   }
}
```

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