Oil & Natural Gas Technology

DOE Award No.: DE-FE 0009963

Quarterly Research Performance Progress Report (Period ending 12/31/2013)

Measurement and Interpretation of Seismic Velocities and Attenuations in Hydrate-Bearing Sediments

Project Period (10/1/2012 to 9/30/2015)

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NETL

Office of Fossil Energy

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Abstract:

Measurement and Interpretation of Seismic Velocities and Attenuations in Hydrate-Bearing Sediments

Grant/Cooperative Agreement DE-FE 0009963.

Progress continues with our project to measure the seismic velocity and attenuation in methane hydrate-bearing sediments. During this last period we focused on developing the pressure equipment for growing hydrates in the CT scanner. Small pressure vessels were constructed from fiberglass-reinforced epoxy, stainless steel, and polyamide-imide (Torlon). All vessels easily withstood test pressures well above the pressures needed to enter the methane hydrate stability field.

- The fiberglass vessel created artifacts in the image due to the irregular distribution of glass fibers

- Thin-walled stainless steel degraded the image of the contained glass beads due to the high density contrast.

- The polyamide-imide vessel provided superior images due to its relatively thin wall, uniform character, and low X-ray attenuation.

Work continues on building the acoustic sensors to measure ultrasonic velocities and attenuations within the vessel.

A “Round-Robin” inter-laboratory test sequence on the effects clays on hydrate-bearing sediment textures and properties is now being designed.

Contents:

Figures:

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Executive Summary:

The purpose of this project is to measure the seismic properties of methane hydrate-bearing sediments and compare these properties to the microscopic textures of the hydrates. A past limitation on our research has been the inability to grow methane hydrates while under observation in the xray tomographic scanner (CT scanner). We strive to document the influence of different formation techniques and environmental conditions.

To reach the methane stability field, low temperatures (less than 10 C) and high pressures (greater than about 13.8 MPa) are needed. Several small vessels were designed and constructed. Vessels must be cycled to pressures at least twice our planned working pressures to ensure safety and leak-proof operation. Several materials were tested.

- Fiberglass reinforced plastic. This material's low density would match the sample and permit faster acquisition.
- Thin-walled stainless steel. A very thin wall may allow sufficient X-ray penetration.
- Polyamide-imide (a.k.a."Torlon") is a high strength polymer well matched to sample density.

All vessels successfully passed pressure tests to at least twice our projected pressure of about 13.8 MPa (2,000 psi). The Torlon vessel was purposefully taken to failure and cracked at 59.2 MPa (8,500 psi). The materials were unequal when used in the CT scanner

- The fiberglass vessel allowed good imaging of the contained bead pack. However, because of the irregular distribution of glass fibers, imaging artifacts occurred degrading the results.

- The thin-walled stainless steel vessel allowed close operation of the X-ray source and detector. However, the high density contrast between the wall and contained bead pack degraded the image.

- The Torlon vessel provided superior images. This is due to the relatively thin wall of this material, it's fine, uniform internal character, and low X-ray attenuation and density match to the bead pack.

During this last period, Dr. Marisa Rydzy completed and defended her doctorial research. Her thesis is available on request.

Accomplishments

Background Requirements

We plan to form methane hydrate as a continuation of our experiments with tetrahydrofuran (THF) hydrate. Thus, elevated pressures are necessary. We have been testing several possible materials for a pressure vessel to be used inside the micro X-ray CT scanner. The formation of methane hydrate requires pressures well above the blue curve in Figure 1. We are further working on a cooling system for the CT scanner. Our idea is to use nitrogen cooling: a fluid line connected to a nitrogen cylinder will blow nitrogen on the outside of the pressure vessel. We will have to adjust the pressure according to the achieved amount of cooling. The pressure should be about 6.9 MPa (1000 psi) above equilibrium pressure (e.g. 1670 psi at 5°C, 3425 psi at 15°C) to ensure the formation of methane hydrate.

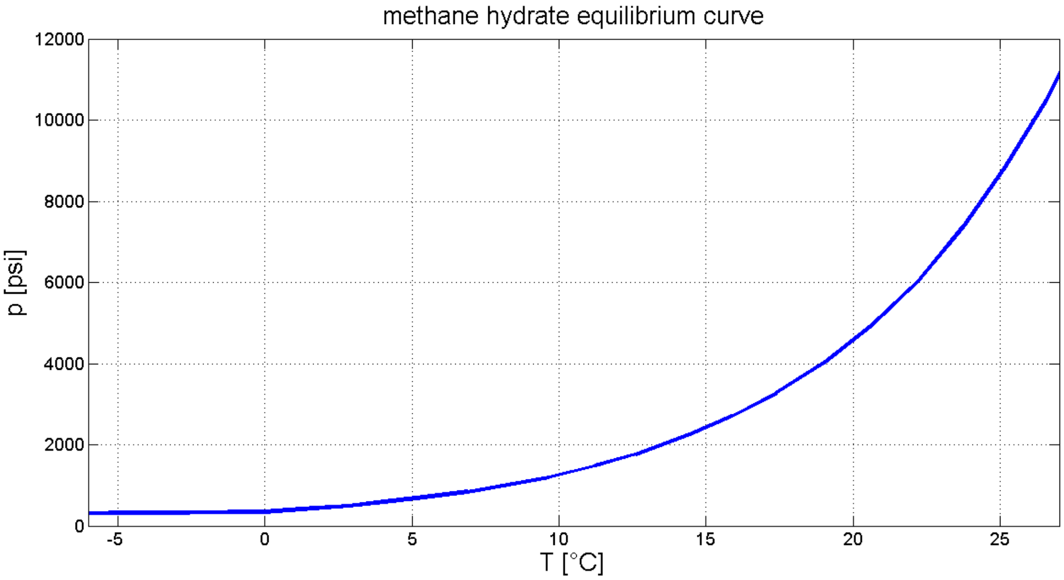


Figure 1: The blue curve shows methane hydrate equilibrium. Methane hydrate is stable at pressures and temperatures above the blue curve (data from Sloan and Koh, 2008)

Materials and Test Results

The tested materials are: fiberglass, stainless steel and Torlon, a polymer. Fiberglass has been successfully pressure tested past 34 MPa (5,000 psi) and stainless steel up to 70 MPa (10,000 psi).

A high strength, low density material was desired for our use, and a potential material was polyamide-imide, also known as Torlon. The physical characteristics of Torlon are listed in Table 1. The Torlon vessel was purposefully taken to failure at 58.6 MPa (8,500 psi), which is well above the required pressure. The resulting crack will be seen in Figures 4 to 6. From the pressure test, we conclude that all three materials are suitable for use inside the CT scanner.

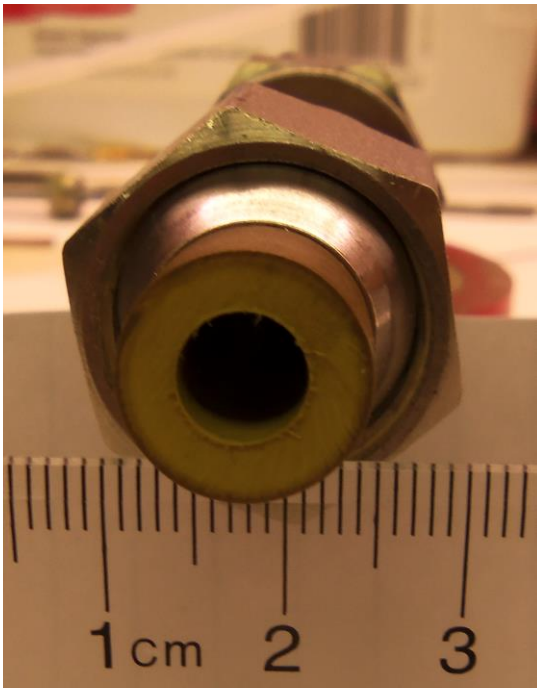


Figure 2. End view of the Torlon (micro-) pressure vessel prior to pressure testing.

Further, CT scans on glass bead samples inside the three different materials were performed in order to find out which material results in highest image quality at lowest scanning time (Figures 4 to 7). Details about the scanning parameters can be found in Table 2. Four different types of scans were performed on each vessel: high and low image quality scans for a small field of view (FOV) at 0.5X, scans with a bigger FOV at 0.5X in order to image the whole pressure vessel, and scans at 4X to determine differences in scanning time for high resolution. The scans with low image quality (as a result of large angular increment) were performed to determine the minimum scanning time required to obtain an image (Figure 4). It has been shown that images at low quality (high amount of noise) can be obtained within 15 minutes. However, for quantitative analysis of CT images, noise should be minimized. Thus, we also obtained test scans at smaller angular increments (Figures 3 to 7).

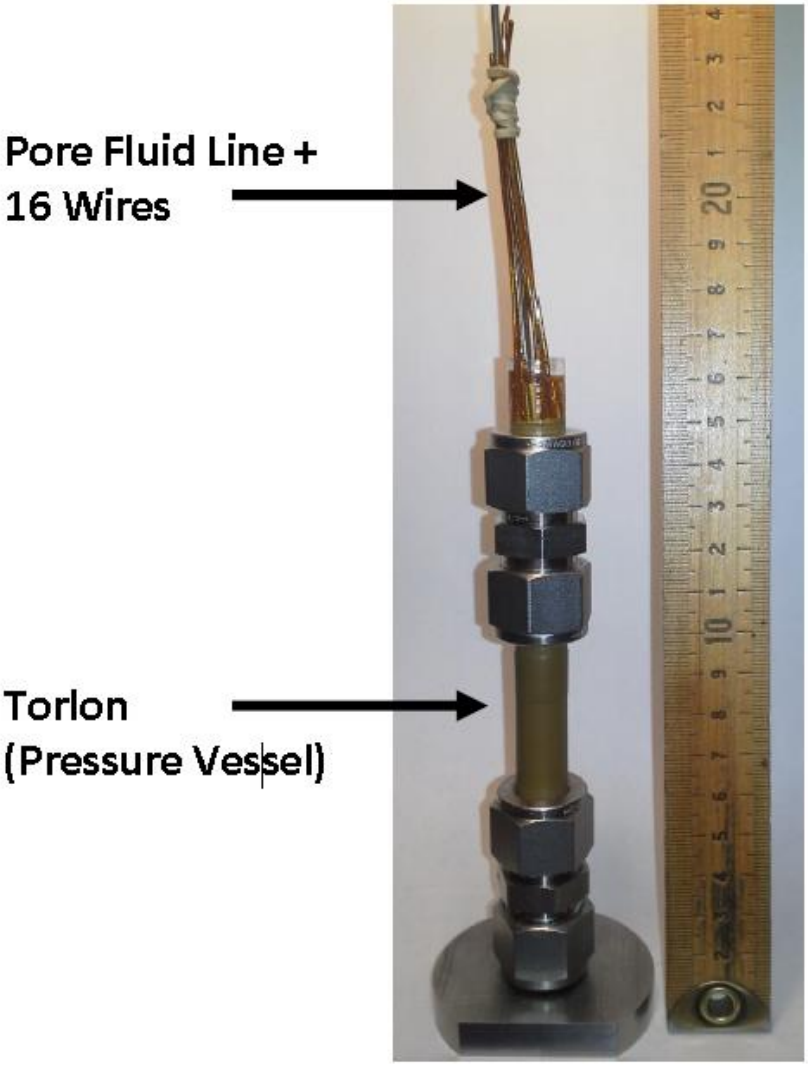
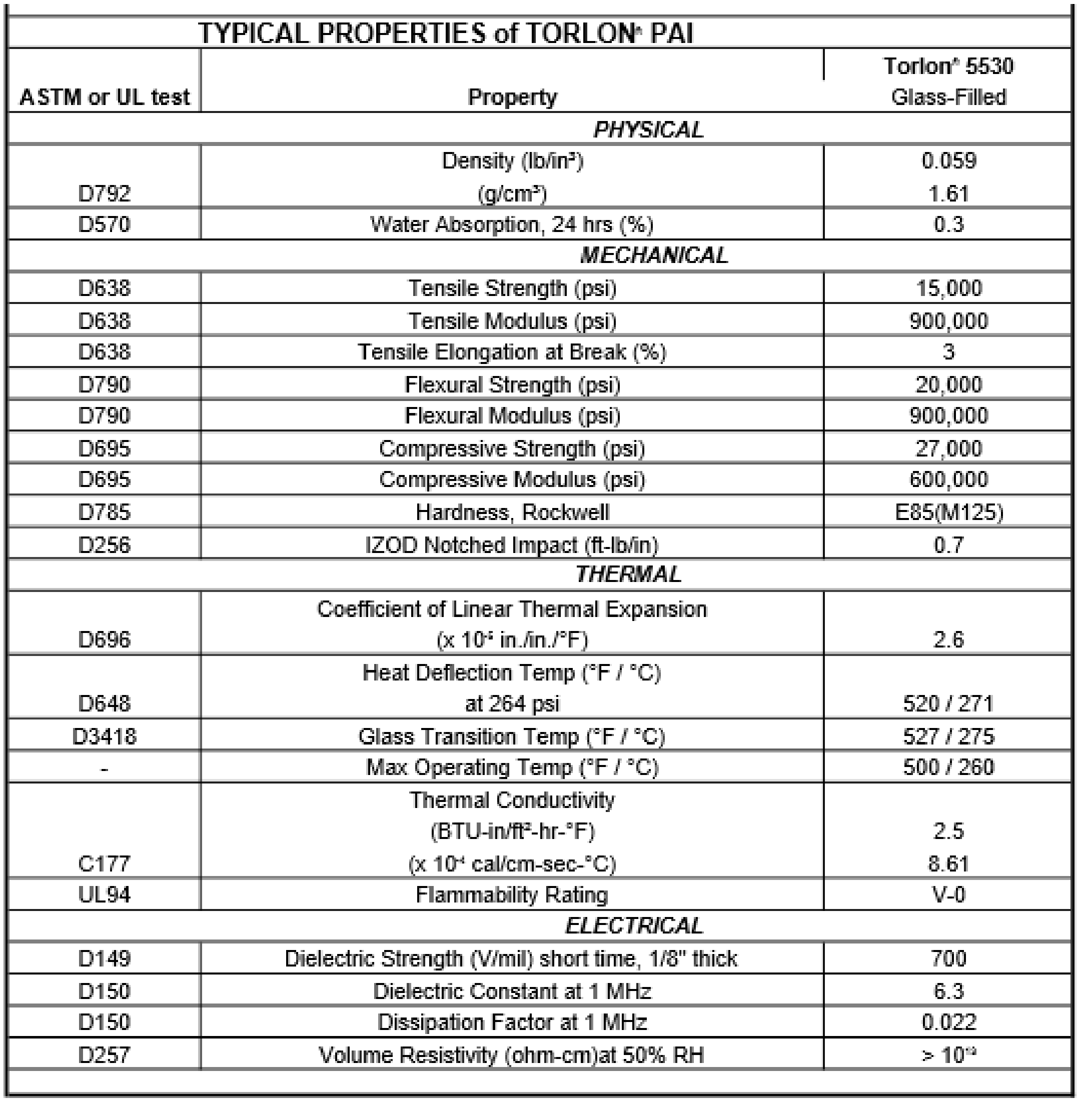


Figure 3. Side view, Torlon vessel with pressure fittings. Note top interface which will permit numerous electronic and fluid connections to sample.

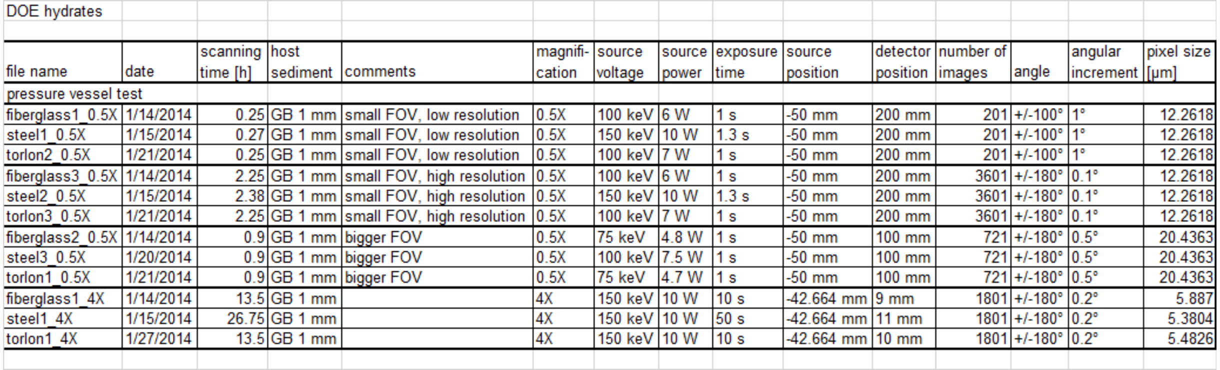


TYPICAL PROPERTIES of TORLON® PAI		
ASTM or UL test	**Property**	**Torlon® 5530 Glass-Filled**
	PHYSICAL	
D792	Density (lb/in³) (g/cm³)	0.059 1.61
D570	Water Absorption, 24 hrs (%)	0.3
	MECHANICAL	
D638	Tensile Strength (psi)	15,000
D638	Tensile Modulus (psi)	900,000
D638	Tensile Elongation at Break (%)	3
D790	Flexural Strength (psi)	20,000
D790	Flexural Modulus (psi)	900,000
D695	Compressive Strength (psi)	27,000
D695	Compressive Modulus (psi)	600,000
D785	Hardness, Rockwell	E85(M125)
D256	IZOD Notched Impact (ft-lb/in)	0.7
	THERMAL	
D696	Coefficient of Linear Thermal Expansion (x 10^{-5} in./in./°F)	2.6
D648	Heat Deflection Temp (°F / °C) at 264 psi	520 / 271
D3418	Glass Transition Temp (°F / °C)	527 / 275
-	Max Operating Temp (°F / °C)	500 / 260
C177	Thermal Conductivity (BTU-in/ft²-hr-°F) (x 10^{-4} cal/cm-sec-°C)	2.5 8.61
UL94	Flammability Rating	V-0
	ELECTRICAL	
D149	Dielectric Strength (V/mil) short time, 1/8" thick	700
D150	Dielectric Constant at 1 MHz	6.3
D150	Dissipation Factor at 1 MHz	0.022
D257	Volume Resistivity (ohm-cm)at 50% RH	> 10^{13}

Table 1. Polyamide-imide (Torlon) physical characteristics.

The test scans showed differences in scanning time. While the required scanning times are almost similar for all 0.5X scans, the scanning time at 4X almost doubled for the stainless steel vessel. Fiberglass and Torlon each require an exposure time of 10 seconds per scan at 4X, stainless steel requires 50 sesconds, resulting in scanning times of 13.5 hours for fiberglass and Torlon and 26.75 hours for stainless steel when all other scanning parameters are kept constant. Moreover, the scans of the stainless steel vessel showed an increased noise level and artifacts in the outer part of the sample close to the vessel. Both can be attributed to the high density of stainless steel. Thus, we conclude that stainless steel is not a proper material for use in the CT scanner.

The observed quality differences between fiberglass and Torlon are minor. It should be noted that the sample in the fiberglass vessel was water saturated while the sample in the Torlon vessel had to be dry (due to the crack from the pressure test). This difference in pore fluid is the reason for the lower contrast between glass beads and pore space in the fiberglass vessel (Figures 4 to 7). The smaller thickness of the fiberglass vessel allows to positition source and detector slightly closer to the sample. This results in higher resolution and shorter scanning times for magnifications of 4X and higher. Thus, fiberglass was initially chosen as a vessel material. However, the uniform nature of the Torlon vessel and low contrast indicated that this material is superior for our experiments.



DOE hydrates

file name	date	scanning time [h]	host sediment	comments	magnifi-cation	source voltage	source power	exposure time	source position	detector position	number of images	angle	angular increment	pixel size [µm]
pressure vessel test														
fiberglass1_0.5X	1/14/2014	0.25	GB 1 mm	small FOV, low resolution	0.5X	100 keV	6 W	1 s	-50 mm	200 mm	201	+/-100°	1°	12.2618
steel1_0.5X	1/15/2014	0.27	GB 1 mm	small FOV, low resolution	0.5X	150 keV	10 W	1.3 s	-50 mm	200 mm	201	+/-100°	1°	12.2618
torlon2_0.5X	1/21/2014	0.25	GB 1 mm	small FOV, low resolution	0.5X	100 keV	7 W	1 s	-50 mm	200 mm	201	+/-100°	1°	12.2618
fiberglass3_0.5X	1/14/2014	2.25	GB 1 mm	small FOV, high resolution	0.5X	100 keV	6 W	1 s	-50 mm	200 mm	3601	+/-180°	0.1°	12.2618
steel2_0.5X	1/15/2014	2.38	GB 1 mm	small FOV, high resolution	0.5X	150 keV	10 W	1.3 s	-50 mm	200 mm	3601	+/-180°	0.1°	12.2618
torlon3_0.5X	1/21/2014	2.25	GB 1 mm	small FOV, high resolution	0.5X	100 keV	7 W	1 s	-50 mm	200 mm	3601	+/-180°	0.1°	12.2618
fiberglass2_0.5X	1/14/2014	0.9	GB 1 mm	bigger FOV	0.5X	75 keV	4.8 W	1 s	-50 mm	100 mm	721	+/-180°	0.5°	20.4363
steel3_0.5X	1/20/2014	0.9	GB 1 mm	bigger FOV	0.5X	100 keV	7.5 W	1 s	-50 mm	100 mm	721	+/-180°	0.5°	20.4363
torlon1_0.5X	1/21/2014	0.9	GB 1 mm	bigger FOV	0.5X	75 keV	4.7 W	1 s	-50 mm	100 mm	721	+/-180°	0.5°	20.4363
fiberglass1_4X	1/14/2014	13.5	GB 1 mm		4X	150 keV	10 W	10 s	-42.664 mm	9 mm	1801	+/-180°	0.2°	5.887
steel1_4X	1/15/2014	26.75	GB 1 mm		4X	150 keV	10 W	50 s	-42.664 mm	11 mm	1801	+/-180°	0.2°	5.3804
torlon1_4X	1/27/2014	13.5	GB 1 mm		4X	150 keV	10 W	10 s	-42.664 mm	10 mm	1801	+/-180°	0.2°	5.4826

Table 2. X-ray scan parameters used to compare vessel materials

Plans

Our plans for thenext period are several fold:

- Increase the inside working space of the test vessel to accommodate sensor components

- Build both acoustic transducers and electrodes that will operate in our vessel

- Conduct parallel Nuclear Magnetic Resonance (NMR) measurements in our Torlon vessels to monitor hydrate growth and disassociation.

Fiberglass ***Stainless Steel*** ***Torlon***

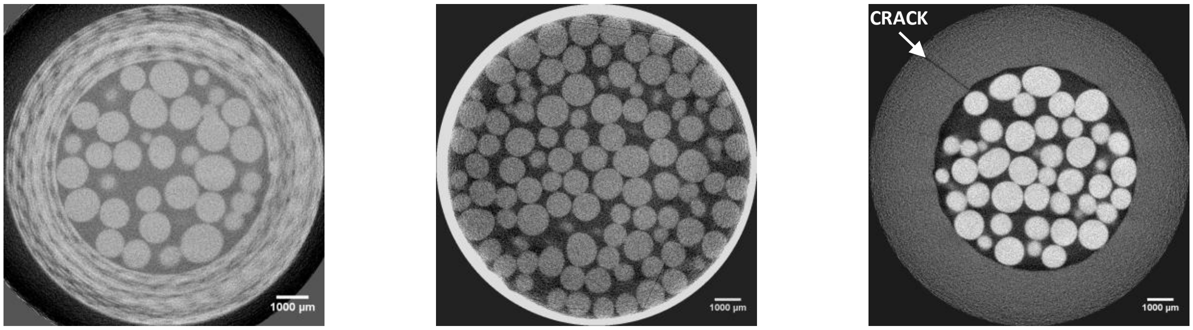


Figure 4. Magnification 0.5X, 201 images (angular increment 1°), small Field of View (FOV)

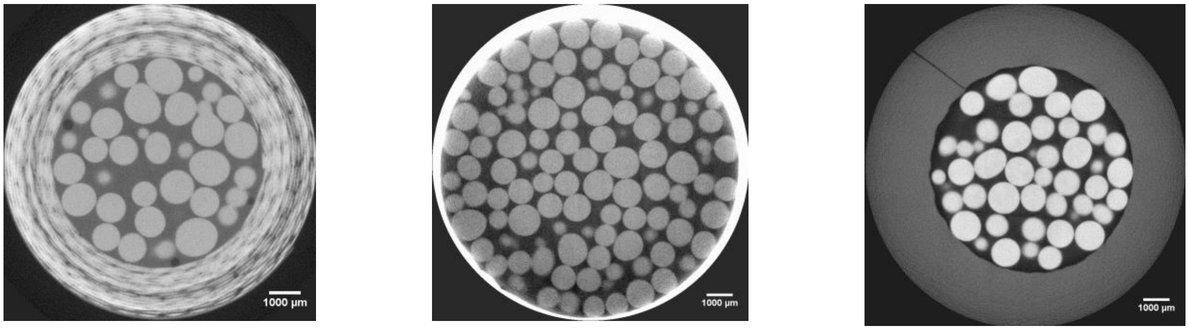


Figure 5. Magnification 0.5X, 3601 images (angular increment 0.1°), small FOV

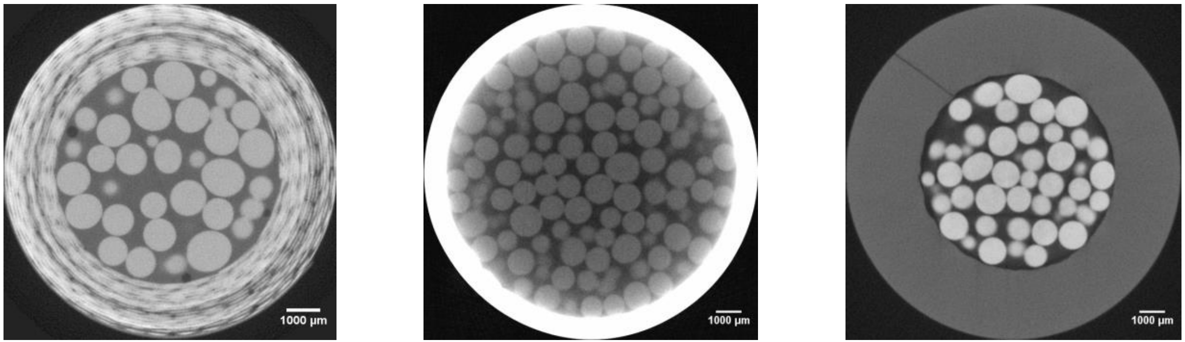


Figure 6. Magnification 0.5X, 721 images (angular increment 0.5°), bigger FOV

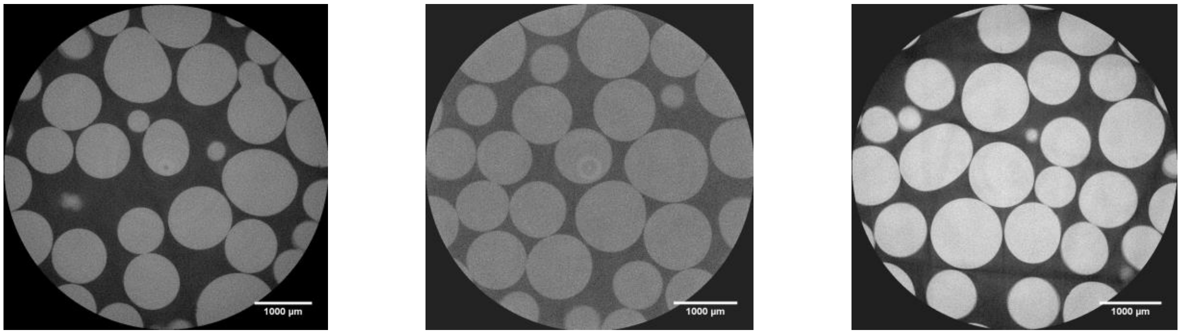


Figure 7. Magnification 4X, 1801 images (angular increment 0.2°)

Participants and Collaborating Organizations

Name: George Radziszewski
Project Role: Research Faculty
Nearest person month worked this period: 1.5
Contribution to Project: Dr. Radziszewski spent his time establishing standards and procedures for running the MicroCT scanner .
Funding Support: “Organics, Clays, Sands and Shales (OCLASSH) consortium
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: N/A
Travelled to foreign country: Yes
If traveled to foreign country(ies): Poland
Duration of stay: 2 weeks

Name: Mathias Pohl
Project Role: Graduate Student
Nearest person month worked this period: 3
Contribution to Project: Mr. Pohl prepared samples and collected ultrasonic data.
Additional Funding Support: N/A
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: N/A
Travelled to foreign country: No
If traveled to foreign country(ies),
duration of stay: N/A

Name: Mandy Schindler
Project Role: Graduate Student
Nearest person month worked this period: 3
Contribution to Project: Ms Schindler prepared samples and collected CT data.
Additional Funding Support: N/A
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: N/A
Travelled to foreign country: No
If traveled to foreign country(ies),
duration of stay: N/A

Name: Weiping Wang
Project Role: Laboratory Technician
Nearest person month worked this period: 0 (just started involvement)
Contribution to Project: Mr. Wang assisted in equipment fabrication
Additional Funding Support: N/A
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: N/A
Travelled to foreign country: Yes

If traveled to foreign country(ies), N/A
duration of stay: N/A

Name: Michael Batzle
Project Role: Principle Investigator
Nearest person month worked: 1
Contribution to Project: Overall (dis)organization.
Funding Support: Academic faculty
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: N/A
Travelled to foreign country: N/A
If traveled to foreign country(ies):

External Collaborations:
Dr. Tim Collett
US Geologic Survey
Denver, Colorado: (if foreign location list country)
Support: Data and guidance on interpretation and application
Tim continues to publish numerous papers on hydrate properties

Changes / Problems

Dr. Marisa Rydzy has successfully defended her PhD thesis December 4, 2013. She is now employed by Shell Inc. in Houston. Her thesis is public and available. No inter

Special Reporting Requirements

None

Budgetary Information

Attached separately

References

Sloan, E. D. & Koh, C. A. (2008), *Clathrate Hydrates of Natural Gases*. 3rd ed., CRC Press, Taylor & Francis Group, Boca Raton, FL

Milestone Status

Measurement and Interpretation of Seismic Velocities and Attenuations in Hydrate-Bearing Sediments
DOE Award No.: DE-FE 0009963

	Milestone Title / Description	Planned Completion Date	Actual Completion Date	Verification Method	Comments
1	Project Management Plan (PMP)	1-Dec-12	28-Nov-12	DOE acceptance	Complete and approved
2	Modifications to low frequency system	1-Jun-13			Complete
3	Modeling established using EOS	31-May-13			Complete
4	Property models of hydrates complete	31-May-13			Continuing
5	Logs acquired and database estab.	31-Dec-13			Continuing
6	THF hydrate grown in pressure vessel	1-Jun-14			Ahead of schedule
7	Methane hydrates from free gas phase	31-Dec-14			On Schedule
8	Methane hydrates from gas in solution	30-Jun-15			Planned
9	CO_2 replacing methane in hydrates	30-Sep-15			Planned
10	MXCT scans completed	30-Sep-15			Continuing
11	Effective media models complete	30-Sep-15			Planned
12	Comparison to in situ data complete	15-Oct-15			Planned
13	Information Dissemination	31-Dec-15			Continuing