

Oil & Natural Gas Technology

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**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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Abstract:

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

Grant/Cooperative Agreement DE-FE 0009963.

Our hydrate project is progressing well in line with our project goals and schedule.

- The low frequency measurement system has been updated
 - o New temperature control system has been installed
 - o New data acquisition software has been developed

- Phase behavior of various hydrates are investigated
 - o Influence of BaCl₂ content in water analyzed
 - o Cyclopentane hydrate formation used as another analog for methane hydrate

- CT scans of loose beads and sediments with THF hydrate have continued to calibrate image analysis of materials. Porosities and water saturations can be calculated directly from the images. Hydrate disassociation is directly observed.

Contents:

Disclaimer 2

Abstract 3

Contents 4

Figures 5

Executive Summary 6

Accomplishments 7

 A. Low Frequency Device 7

 B. Phase Behavior and Characterization 12

 C. MXCT imaging 14

Participants and Collaborating Organizations..... 17

Changes / Problems 18

Special Reporting Requirements 18

Budgetary Information 18

References 19

Appendices:

Appendix I.

Milestone Schedule 20

Figures:

Figure 1. Temperature bath and insulation on the Low Frequency Device	7
Figure 2. Labview data acquisition screen	8
Figure 3. Fox Hills sandstone sample preparation	9
Figure 4. Sample holder for pure THF hydrate measurements	9
Figure 5. Low Frequency Device	11
Figure 6. Sample mounted in the Low Frequency Device	11
Figure 7. Differential Scanning Calorimetry (DSC) of THF hydrate	13
Figure 8. THF phase equilibrium shift with BaCl ₂	13
Figure 9. CT scans of THF hydrate disassociation	14
Figure 10. Porosity calculations from CT scans	16
Figure 11. Calculation of water saturation from CT scans	16

Executive Summary:

The goal of this project is to measure and understand seismic attenuation and velocity in hydrate-bearing sediments. Specifically, measurements must be made in the seismic frequency band (3 – 2000 Hz) to be valid for interpretation. In addition, very broad band measurements are required to understand the physical mechanisms responsible. Our samples also must be prepared to duplicate hydrates in nature. This requires characterization of the hydrate formation and disassociation process.

The low frequency device has been modified and updated for hydrate measurement. A new low temperature bath has been obtained and installed. This cooling capability allows us to reach below zero °C and remain at temperature with stability. The data acquisition system also needed to be upgraded to improve the stability of the system and reduce the time required for an acquisition sequence. New digitizing equipment was installed and controlling software developed. Comparison tests are now being conducted.

The phase equilibrium behavior must be established for hydrates under our experimental conditions. Most experiments will be conducted under temperature and pressure conditions that permit stable hydrate formation, but prevent ice formation. Xray imaging will provide direct observation of the hydrate location. Unfortunately, the density of water and hydrates are almost equal, making imaging very difficult. Thus, in order to image the hydrates in sediment, a doping compound such as BaCl₂ must be used to increase contrast. However, adding another compound to the water phase will alter the temperature and pressure conditions for phase stability. Calculations of THF stability with 5 wt% BaCl₂ were made based on comparison with salt effect on the water-ice transition. 5 wt% BaCl₂ is expected to lower the transition temperature by about 1 °C. The freezing point of the remaining salt water solution will be lowered by 7.7 °C. Differential Scanning Calorimetry (DSC) was performed on THF hydrate-water (and ice) mixtures to provide the direct measurement to confirm the calculations. Additional calculations are underway for cyclopentane hydrate stability.

The Micro CT scanner images are being collected to characterize the texture and location of hydrates forming in sediments and glass beads. THF hydrate disassociation over time lengths as long as 144 minutes are documented. Similar images can be used to calculate sample porosity. Water saturation is another parameter that could be obtained from the CT images. For both of these attributes, calibration is required to establish proper data reduction procedures. Various “.tif” format images will be made available over our website.

Accomplishments

A. Low Frequency System

One of our primary goals is to measure the seismic attenuations and velocities within the exploration frequency band. This requires a specific set of equipment for measurement of elastic properties over a broad range. In addition, measurements must be made at very low amplitudes to be valid. To adapt this system to measure hydrates, temperature control and data acquisition required improvement.

To allow temperature control, we installed a new cooling bath. We also improved the existing insulation. The resulting system is shown in Figure 1. The new temperature system was tested successfully and temperatures below 0 °C were reached, which are sufficient for hydrate formation.

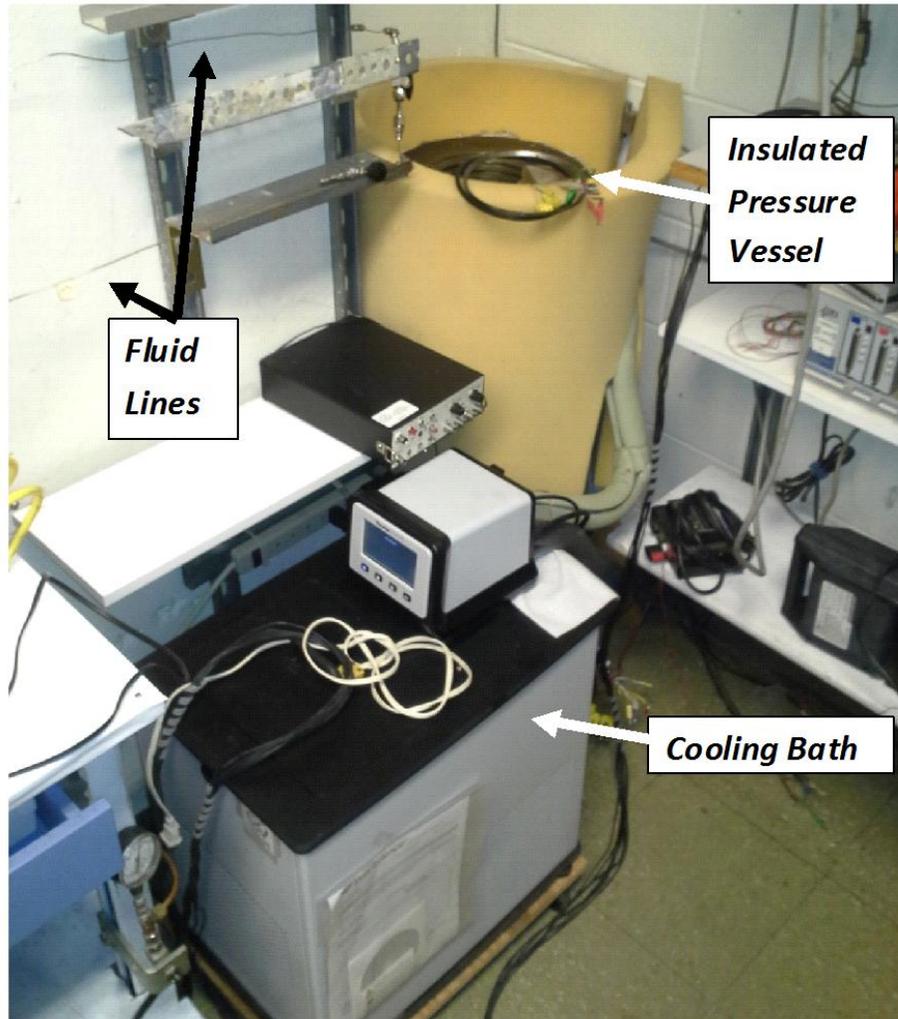


Figure 1: Insulated pressure vessel and cooling bath. This setup has been tested and temperatures can be controlled below freezing conditions.

Previously, the data acquisition system involved three phase lock amplifiers. These amplifiers measures both amplitude and phase of sinusoidal signals output from the sample assembly. Strain channels were switched through the amplifiers sequentially and data was then transferred to the computer via an IEE 488 bus. Unfortunately, these amplifiers were not robust and often either stopped communicating with the computer or failed completely. In addition, a typical acquisition point required three hours.

To improve this acquisition process, a new acquisition system was developed using a digitizing board from National Instruments. Data is acquired simultaneously at high resolution. The acquisition process is now controlled by a Labview program interface with the hardware. An example screen is shown in Figure 2. A complete sweep of frequencies now takes approximately 20 minutes (dominated by the low frequencies).

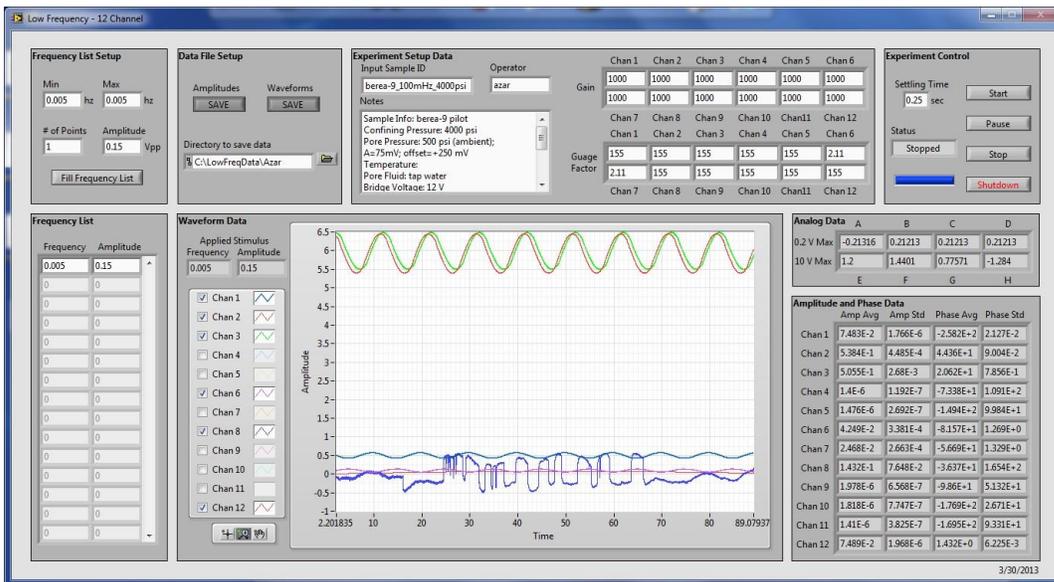


Figure 2. Labview screen controlling data acquisition.

Low frequency velocity and attenuation measurements will be performed on THF hydrate-bearing sandstone and pure THF hydrate. In preparation of the velocity measurements, three Foxhill sandstone samples have been prepared (Figure 3). In addition, a sample holder was constructed that allows low-frequency velocity measurements in pure THF hydrate (Figure 4), which represents one end member of our sediment-hydrate-pore water system. Measuring the elastic properties of THF hydrate without sediment will provide us with examples of velocities and losses within the hydrates themselves. These data will provide the raw information needed to build our petrophysical modeling.

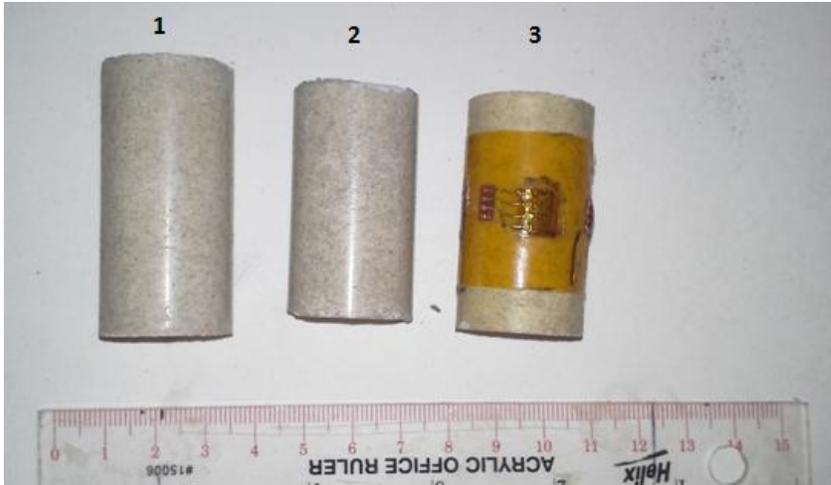


Figure 3: Prepared Fox Hill Sandstone samples, 1-2) coated with a thin layer of epoxy 2) coated with a thin layer of epoxy 3) strain gages have been glued to the sample

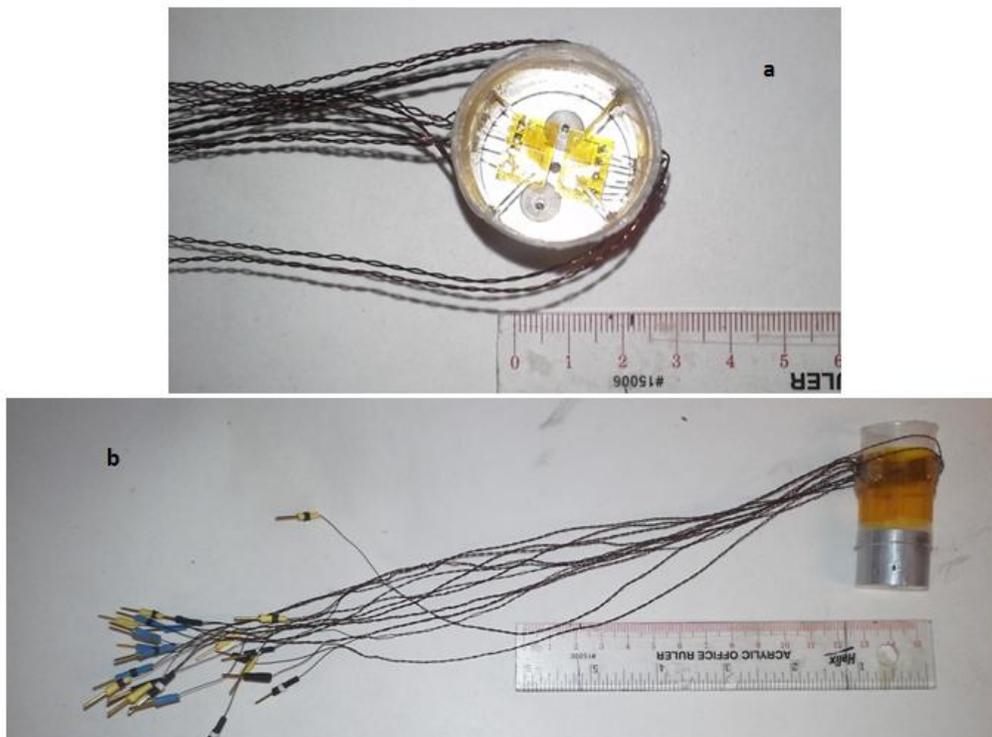


Figure 4. a) Sample holder for pure THF hydrate low frequency measurements (top view)
b) Side view of sample holder for pure THF hydrate measurements

Fox Hill Sandstone has been chosen as a representative for marine sediments because of it is of high-porosity (28.8 %) and loosely consolidated. Also to perform our experiments we needed a sample that has some matrix strength so we are able to attach our strain gages. It is made up of fine to medium grains and has a mean grain size of 0.21 mm (upper fine sand). It consists mostly of quartz (73 %). The main clay mineral is kaolinite (8 %) which is a non-swelling clay mineral to prevent pore pressure build up due to clay swelling.

Careful preparation is required to properly construct a sample and gather valid data. The following procedure is followed:

- Cutting an one inch diameter sample
- Adding a thin layer of water resistant epoxy
- Smoothing the surface using sandpaper
- Adding a layer of kapton foil to prevent nitrogen leakage
- Gluing strain gages on top of the kapton
- Connecting wires to the gages
- Gluing aluminum standard transducers to the top and bottom of the sample
- Sealing the complete sample with soft epoxy

The prepared specimen will be installed in the measurement assembly as shown in Figure 5 and 6. A uniaxial sinusoidal stress at discrete frequencies (2-2000 Hz) is applied by a shaker on the bottom of the sample. A function generator produced a signal which drove the shaker. The strain gages then measured the resulting strains.

The assembly is located inside a temperature-controlled pressure vessel (Figure 5). Fluid ports allow fluid injection into the sample. One digital pump is used to control the pore pressure. The confining pressure is applied using nitrogen gas.

The low-frequency measurement itself is based on the linear stress-strain relationship (Hooke's law). By knowing the exerted stress applied on the sample and the resulting deformation we will calculate Young's modulus, Poisson's ratio, bulk modulus, shear modulus, and compressional modulus, which will be used to calculate the corresponding compressional (p) and shear (s) wave velocities. With our system we will also be able to investigate the attenuation effects based on the phase information

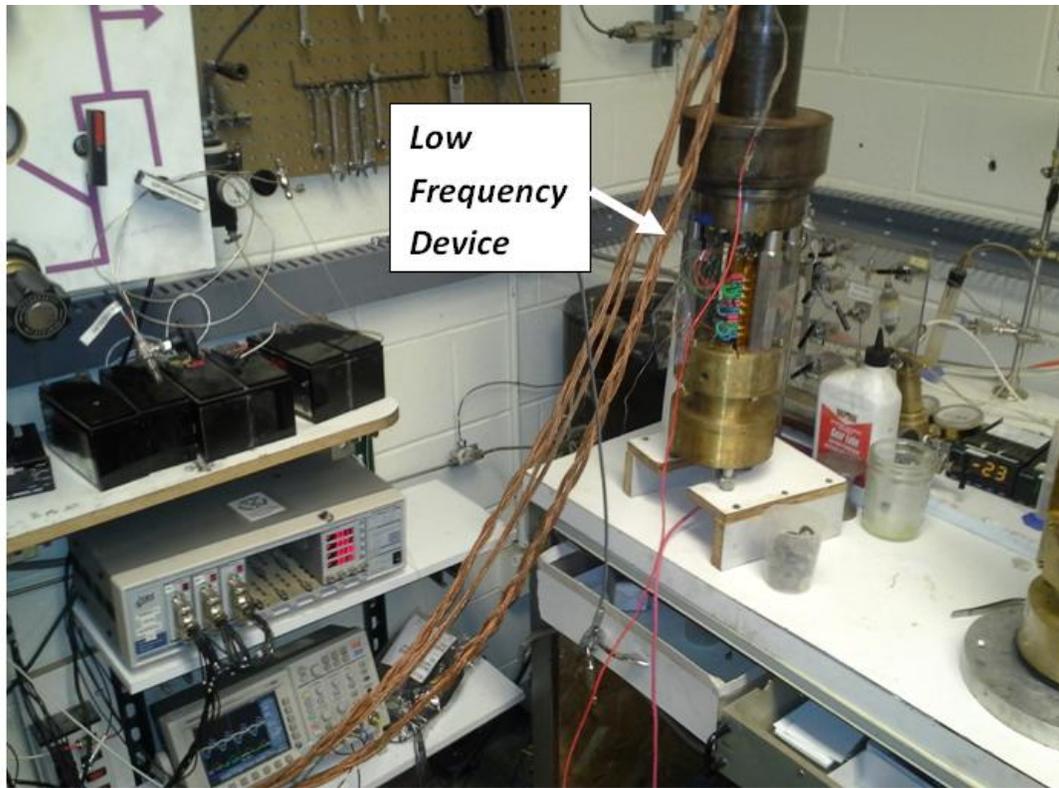


Figure 5. Low frequency device

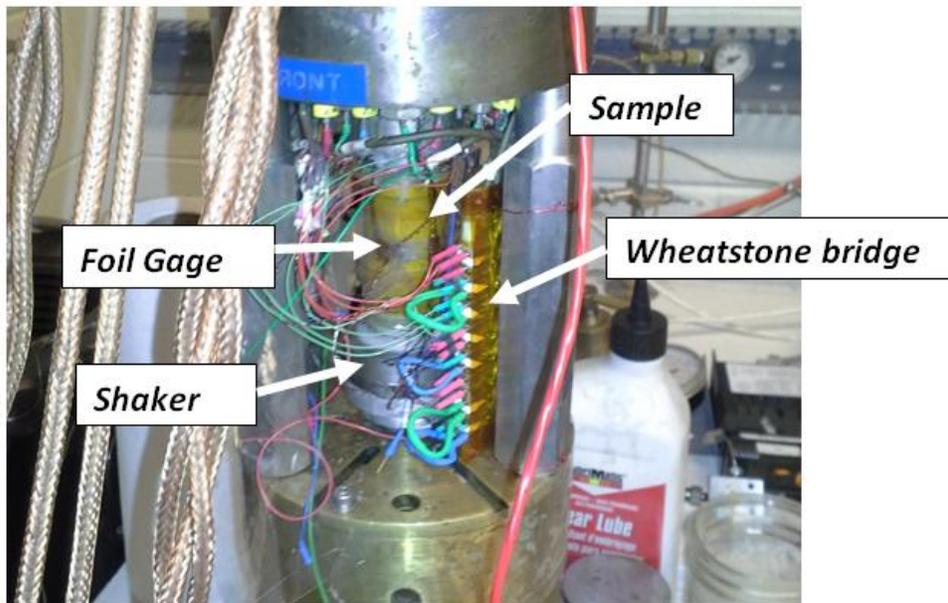


Figure 6. Sample in the low frequency device.

B. Phase Behavior and Characterization

We will be measuring and observing the formation and disassociation of hydrates. However, to observe the hydrates in the CT scanner, there must be a contrast between the water and hydrate phase. Our initial THF-H₂O mixtures contained 10wt% (w.r.t. water) BaCl₂. That amount turned out to be too much, as the resulting Xray absorption for BaCl₂+H₂O turned out to be same as for quartz, which made it impossible to distinguish between sediment grains and BaCl₂+H₂O. Consequently, we reduced the amount of BaCl₂ to 5wt%. Hence, we need the calculated phase changes for 5 wt% BaCl₂.

To provide background information, Differential Scanning Calorimetry (DSC) measurements on THF + BaCl₂ + H₂O mixtures composed of 85% H₂O + 15% THF with and without 5% BaCl₂ were performed (Figure 7). The peak of THF hydrate dissociation for the sample with BaCl₂ was shifted by -1.1 °C compared to the dissociation peak of the sample without BaCl₂ (The peaks were quite broad). Kerkar et al. (2009, Applied Physics Letters 95) stated that they expected THF hydrate stability to be shifted the same amount as would be expected for ice. That shift would be about -1.4 °C for 5wt% BaCl₂ ($DT=K_f \times m \times i$). Figure 8 shows our expected the equilibrium temperatures before and after adding BaCl₂.

Assuming all THF is consumed by hydrate formation, the BaCl₂ concentration of the remaining water would increase to about 30%. The expected freezing point depression can be calculated as -12.4 °C. The peak for fusion of ice in the DSC measurement was at about -7.5 °C (onset was about 9.5 °C). The discrepancy may be attributed to a) we do not have an ideal solution, b) we formed less hydrate and have more water left than expected, c) the presence of hydrate has an effect.

To confirm some of these dependencies, we will perform some additional DSC measurements. We plan to measure the stoichiometric mix (19 wt% THF) to have a baseline as well as (15% THF with an addition of 10 wt% BaCl₂). We are currently, preparing another batch of MXCT samples (15 wt% THF and 5 wt% BaCl₂). Inside one of the small specimens, we placed a thermocouple. The samples were cooled at 1 °C / 90 min. At -0.8 °C an exothermic peak indicated hydrate formation. We will then cool further to achieve ice formation. Afterwards, we will slowly warm the sample back to room temperature. We hope exo- and endothermic peaks will give us better idea about the phase equilibria of ice and water.

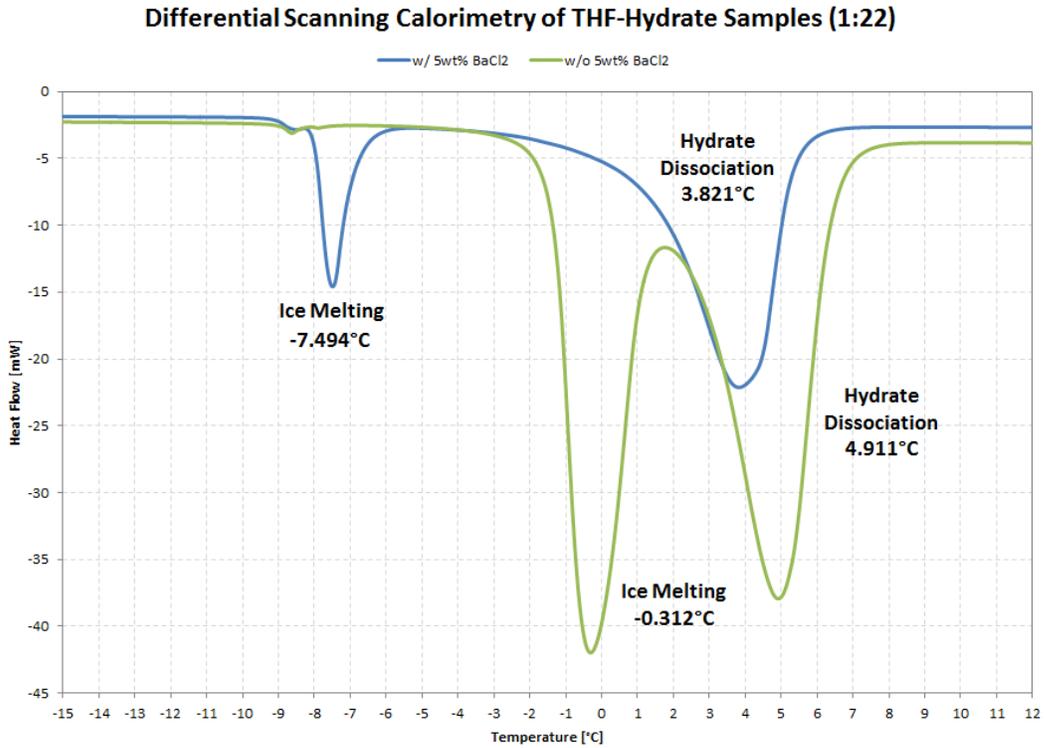


Figure 7. Disassociation of THF hydrate with BaCl₂ (blue line) and without BaCl₂ (green line) as indicated by Differential Scanning Calorimetry (DSC).

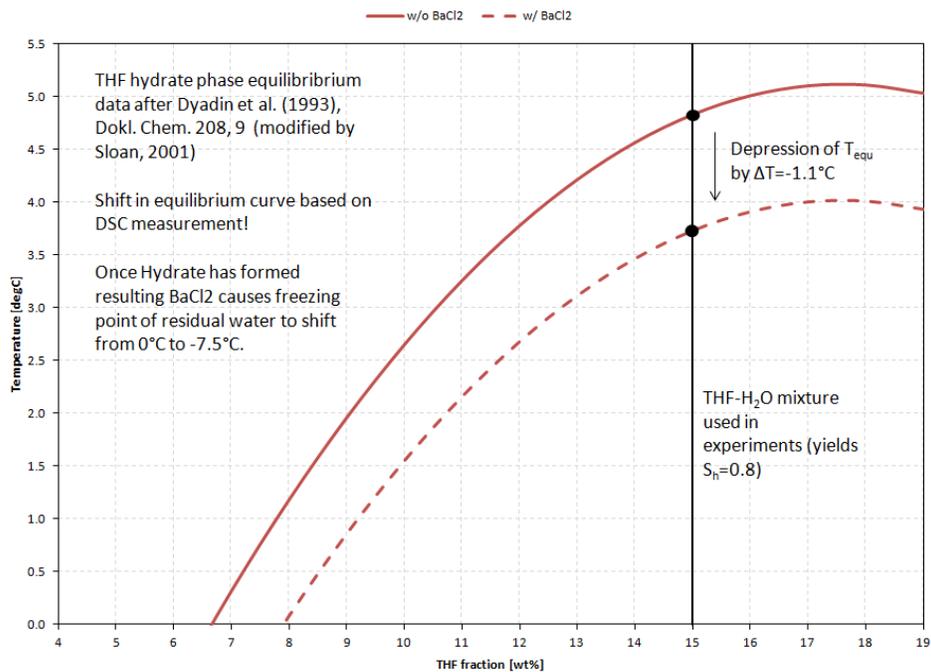


Figure 8. Depression of the hydrate equilibrium temperature associated with BaCl₂ in solution.

C. MXCT imaging

Hydrate-bearing glass bead samples

THF hydrate

The most recent batch of THF-hydrate bearing glass bead samples (THF1-10) has been monitored much more closely during the hydrate-formation. Marisa recorded waveforms to see changes in ultrasonic velocities and thus detect the formation of hydrate in the samples. After the waveforms did not change anymore, i.e. the hydrate formation process was completed, they have been cooled further with liquid nitrogen transforming any remaining water into ice. A thermocouple was inserted directly into one of the samples (previous batches: temperature measured outside of the samples). This way, a certain increase in temperature induced by the exothermic formation of THF hydrate was observed.

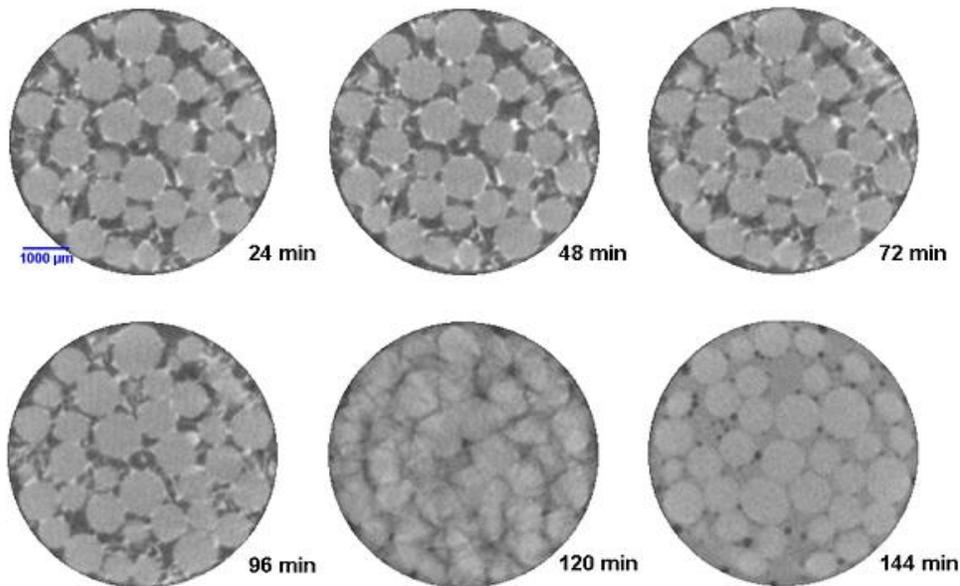


Figure 9. Micro X-ray CT images of dissociating THF hydrate in a glass bead sample

Figure 9 shows the dissociation of THF hydrate in a glass bead sample monitored by micro X-ray CT imaging. To increase the density contrast between ice and THF hydrate, 5 wt% barium chloride was added to all samples. The medium gray spheres depict the glass beads in the sample, the white areas in the pore space represent barium-chloride spiked ice and the dark gray areas in the pore space represent THF hydrate.

The first three tomographies show that both substances – ice and THF hydrate – are stable at initial temperatures. After 96 minutes, the ice starts to melt as indicated by lower gray scale values for the previously white ice-filled areas. After 120 minutes, the substances in the pore space mix due to dissociation of hydrate and melting of ice which is indicated by the blurry appearance of this tomography. After 144 minutes the pore space is filled with a homogenous substance represented by a medium gray value, a mixture of water, barium chloride and THF. The dark spots in this tomography show air bubbles in the sample.

THF hydrate is used as a proxy of methane hydrate formed from methane dissolved in water. The tomographies show ice at the grain surfaces and THF hydrate formed in the pore space with little to no contact to grain surfaces.

Cyclopentane hydrate

While we are not able yet to conduct micro X-ray CT images of methane hydrate, we are trying to find a proxy for methane hydrate formed from the gaseous phase of methane. Since cyclopentane is immiscible with water, it is thought to resemble the macro-scale properties of methane hydrate formed from methane gas [Aspenes *et al.*, 2010]. As opposed to methane hydrate, cyclopentane hydrate forms at atmospheric pressure and can thus be micro X-ray CT imaged with our current setup.

CT scans were acquired for an initial batch of cyclopentane hydrate bearing glass bead samples (CP1 – 8). The samples have been monitored in the same way as previously described for THF hydrate and showed the characteristic increase in ultrasonic velocities as well as a spike in temperatures. Thus, it is indicated that cyclopentane hydrate was formed but due to insufficient density contrast between cyclopentane and cyclopentane hydrate in the pore space the MXCT images do not yet allow any conclusions about the special distribution. We are currently searching for substances that can be added to increase the density of cyclopentane.

Dry and partially water saturated calibration samples: glass beads and F100 Ottawa sand

These calibration measurements will allow the characterization of samples for ultrasonic velocity measurements.

Calculation of porosity and water saturation of glass bead samples are based on stacks of 100 MXCT images (dry_glass_beads_1 – 4, glass_beads+water1 – 3). The calculations are done in *ImageJ* and are based on differences in gray scale values which allow to differentiate among

- glass beads and pore space to calculate porosity
- glass beads, air filled pore space and water filled pore space to calculate water saturation.

Figures 10 and 11 show examples of images used for the calculation of porosity and water saturation.

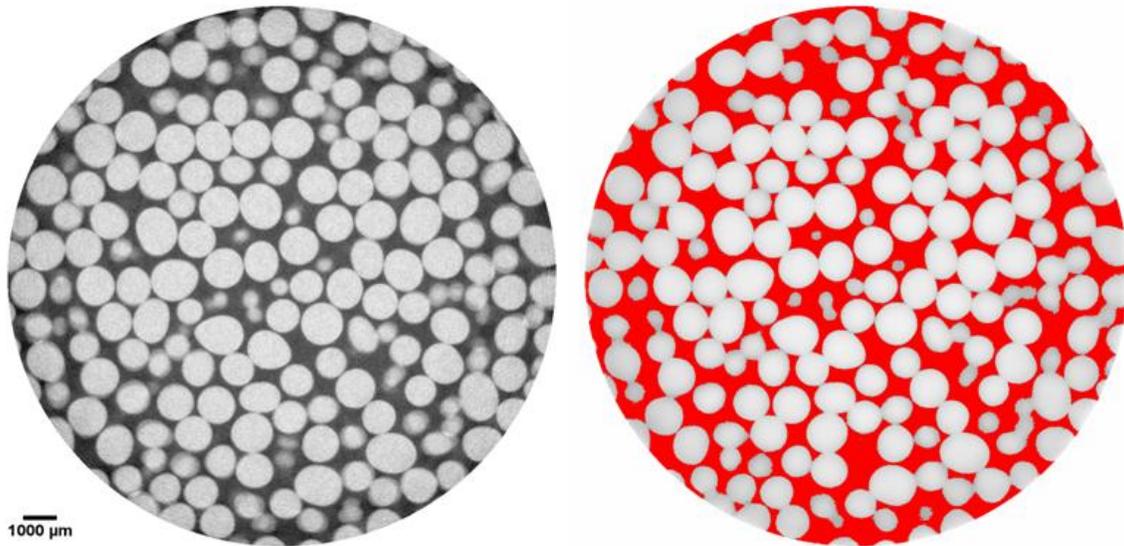


Figure 10. Porosity calculation in sample “dry_glass_beads_4”, left: raw MXCT image, right: processed image with porosity shown in red

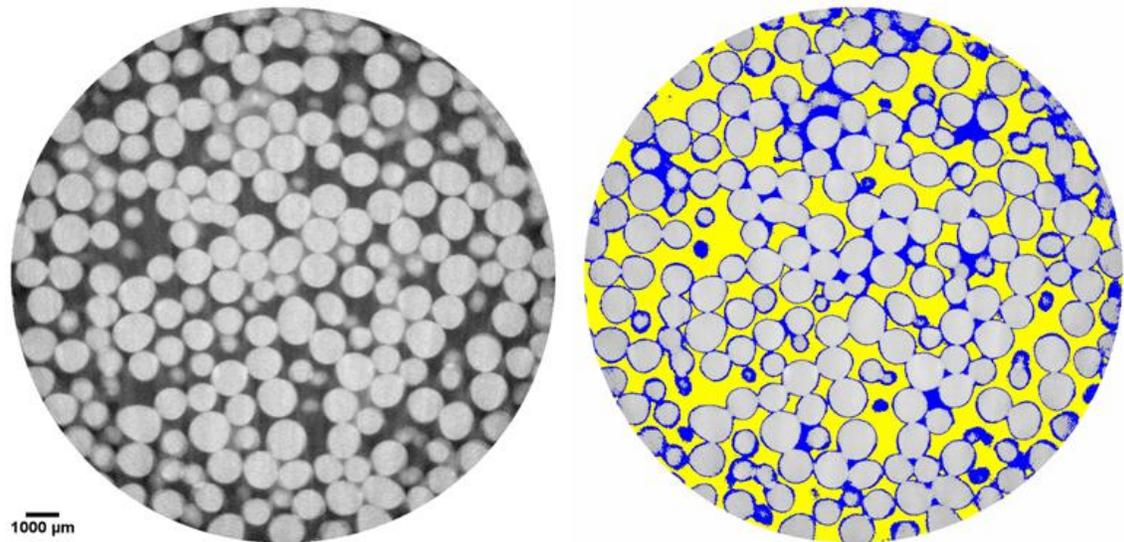


Figure 11. Calculation of water saturation in sample “glass_beads+water3”, left: raw MXCT image, right: processed image with air-filled porosity shown in yellow and water-filled porosity shown in blue.

The calculation of porosity seems to be reliable and shows errors of less than 5%. The MXCT porosities will be compared to porosities obtained by Archimedes method for verification. The calculation of water saturation does still require some refinement. Figure 11 shows that areas around the grain surfaces that can be misinterpreted as water filled porosity due to similar gray scale values which results in a miscalculation of water saturation.

Currently, samples of Ottawa sand F110 with kaolinite contents of 0%, 10% and 30% are scanned to provide further calibration. Mathias will use these images to characterize ultrasonic samples for the planned study on the influence of clay content on hydrate-bearing sediments.

Participants and Collaborating Organizations

Name: George Radziszewski

Project Role: Research Faculty

Nearest person month worked: 1

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: No

If traveled to foreign country(ies):

Name: Marisa Rydzy

Project Role: Graduate Student

Nearest person month worked: 1

Contribution to Project: Ms. Rydzy assisted in design of high pressure low temperature equipment.

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: 1

Contribution to Project: Ms. Schindler assisted in sample preparation

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), (Germany)
duration of stay: 3 weeks

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
(see Collett and Lee, 2011)

Changes / Problems

Nuclear Magnetic Resonance (NMR) measurements are now planned to characterize water content. Entering the hydrate stability region does not necessarily prove that all the appropriate water has converted to hydrates. Non-conversion will be an important influence on our attenuation and velocity measurements and modeling. Fortunately, a new NMR system is available in the petroleum engineering department. Initial measurements on THF hydrate will be performed to quantify and characterize the disassociation process.

Special Reporting Requirements

None

Budgetary Information

Supplied separately

References

- Aspenes, G., L. E. Dieker, Z. M. Aman, S. Høiland, a K. Sum, C. a Koh, and E. D. Sloan (2010), Adhesion force between cyclopentane hydrates and solid surface materials., *Journal of colloid and interface science*, 343(2), 529–36, doi:10.1016/j.jcis.2009.11.071. [online] Available from: <http://www.ncbi.nlm.nih.gov/pubmed/20036368> (Accessed 22 March 2013)
- Karanjkar, P. U., J. W. Lee, and J. F. Morris (2012), Calorimetric investigation of cyclopentane hydrate formation in an emulsion, *Chemical Engineering Science*, 68(1), 481–491, doi:10.1016/j.ces.2011.10.014. [online] Available from: <http://linkinghub.elsevier.com/retrieve/pii/S0009250911007184> (Accessed 22 March 2013)

Appendix 1

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	30-April-13	Measurements	Undergoing tests
3	Modeling established using EOS	31-May-13	10-May-13	Results Rpt	On schedule
4	Property models of hydrates complete	31-May-13			On schedule
5	Logs acquired and database estab.	31-Dec-13			Planned
6	THF hydrate grown in pressure vessel	1-Jun-14			Planned
7	Methane hydrates from free gas phase	31-Dec-14			Planned
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