DOE Award No.: DE-FE-0009963

Quarterly Research Performance Progress Report (Period ending 6/30/2015)

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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Disclaimer

Abstract

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

Grant/Cooperative Agreement DE-FE 0009963.

During this period we included ultrasonic transducers into the MXCT scanner setup. This is a step towards performing ultrasonic velocity measurements and micro X-ray CT imaging simultaneously on hydrate-bearing samples. As a proof-of-concept MXCT images and ultrasonic waveforms are shown for a dry sandstone sample.

We started with the application of our experimental results to in-situ data. This is a step towards the calculation of velocities and attenuation from well logging data of methane-hydrate bearing sediments.

We are building new pressure vessel for the use in both, MXCT and NMR. These will allow us to link the results of our MXCT imaging experiments to our low-field NMR experiments and high-field NMR experiments performed by Arvind Gupta (2007).

- Sonic logs show reduced frequency content within hydrate-bearing layers indicating higher attenuation.

- Frequency content decreases in sonic logs below hydrate-bearing layer but does not recover to values obtained above the hydrate zone. This could be caused by the presence of free gas.

- Ultrasonic P-wave transducers have been built and proven to record waveforms with sufficient signal quality while not interfering with the MXCT imaging.

- Two torlon vessels are currently being built for the use in the MXCT and NMR. It has been shown that it is possible to obtain high-resolution micro CT images despite the attenuation caused by their 8-mm thick walls.

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2. Accomplishments

2.1 Overview of Milestone Status

Our current position is shown in the time chart in Figure 1. In the current period of Q11 (Q3 of Year 3), we continued our work on Task 9 – MXCT Characterization and Task 5 – THF Hydrate-Bearing Rock. We started the work on Task 11 – Comparison with Log Data. Mandy Schindler will defend her second comprehensive exam (thesis proposal) in Q12. With the no-cost extension, the current date for the project to end is April 30, 2016. Thus, technically, the project is in the last phase of the project – Year 3 with efforts devoted towards Tasks 7 - 13.

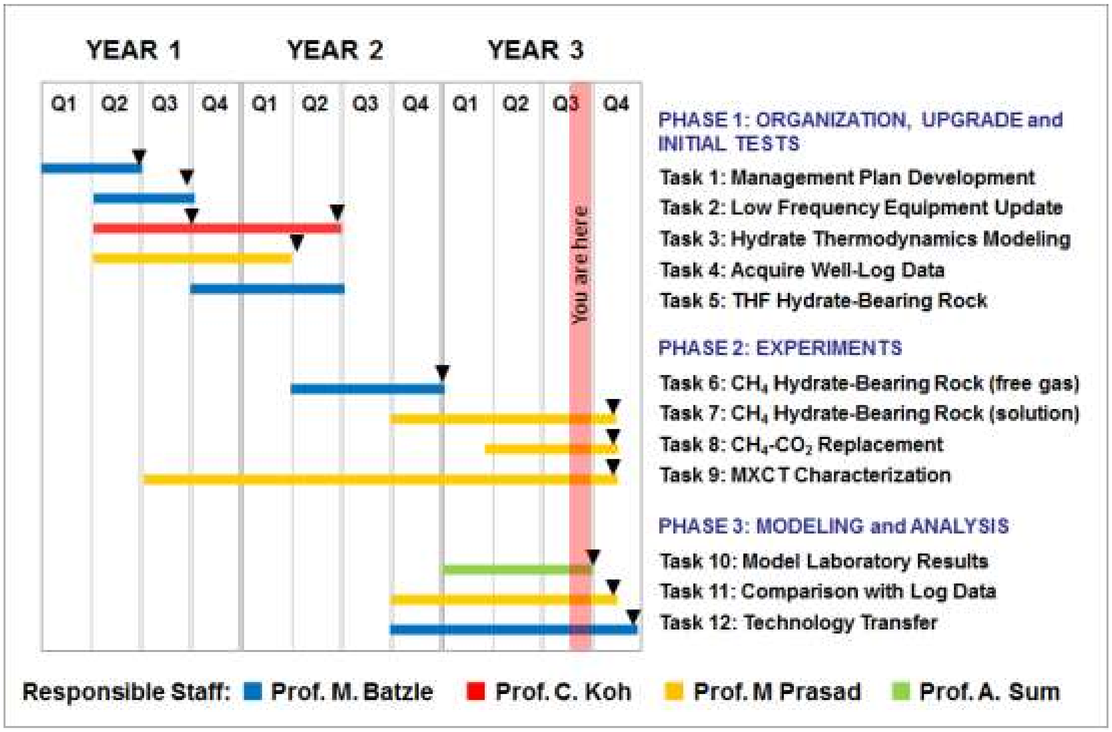

Figure 1. Milestone Status. We are at the end of our eleventh quarter and are approaching the start of the final phase of this project.

Table 1. Milestone status

Mile-stone	Title / Description	Status	Completion date (completed or expected)
Completed			
1	Project Management Plan (PMP)	Complete & approved	1 Dec 2012
2	Modifications to low frequency system	Completed	1 June 2013
3	Modeling established using EOS	Completed	31 May 2014
4	Property models of hydrates completed	Completed	31 May 2014
5	Logs acquired and database established	Completed	15 Jun 2014
6	THF hydrate grown in pressure vessel	Completed	15 Apr 2014
7	Methane hydrates from free gas phase (somewhat behind schedule)	Continuing*	31 Dec 2015
Continuing or Planned			
8	Methane hydrates from gas in solution	Planned	31 Dec 2015
9	CO2 replacing methane in hydrates	Planned	30 Sep 2015
10	MXCT scans conducted	Continuing*	30 Sep 2015
11	Effective media models complete	Planned	30 Sep 2015
12	Comparison to in situ data complete	Planned	15 Oct 2015
13	Information Dissemination	Continuing*	31 Dec 2015
*initial stages were completed on schedule, but the process continues throughout the project			

2.2 Integrating High-Field NMR, Low-Field NMR and MXCT Data

In the coming quarter, we plan to build on the expertise from Carolyn Koh's hydrate group. Experiments by former Ph.D. student, Arvind Gupta (Gupta, 2007) show that methane formation and dissociation in natural sediments show distinct peaks for methane in different cages (Figure 4). The high-field NMR data show the decay of peaks due to methane in the large and small cages, and an increase in the methane gas peak. Similar variations were observed in low-field NMR and acoustic waveform data during dissociation of THF hydrates in sediments.

In the coming quarter, we plan to adapt the high pressure synthesis apparatus developed by Gupta (2007) to measure the dissociation of methane hydrate in sediment systems (Figure 5). The adaptations will include construction of a vessel to make larger methane-hydrate bearing sediment samples while performing acoustic, low-field NMR, and CT imaging during the formation and dissociation process (see Chapter 2.5).

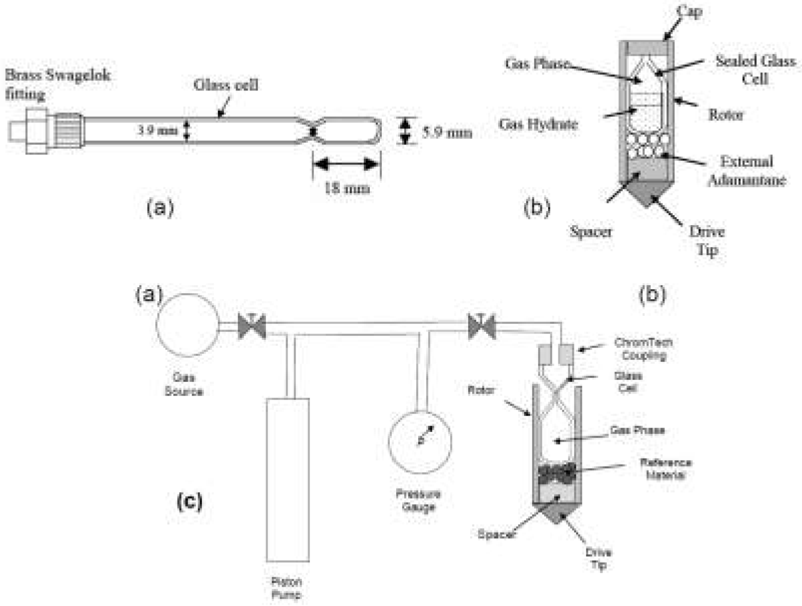

Figure 2. (a). The pyrex glass tube with a brass fitting used to prepare the NMR sample. (b). Zirconium rotor and sealed glass sample cell assembly. (c). Non-spinning sample cell connected to pressure gauge.

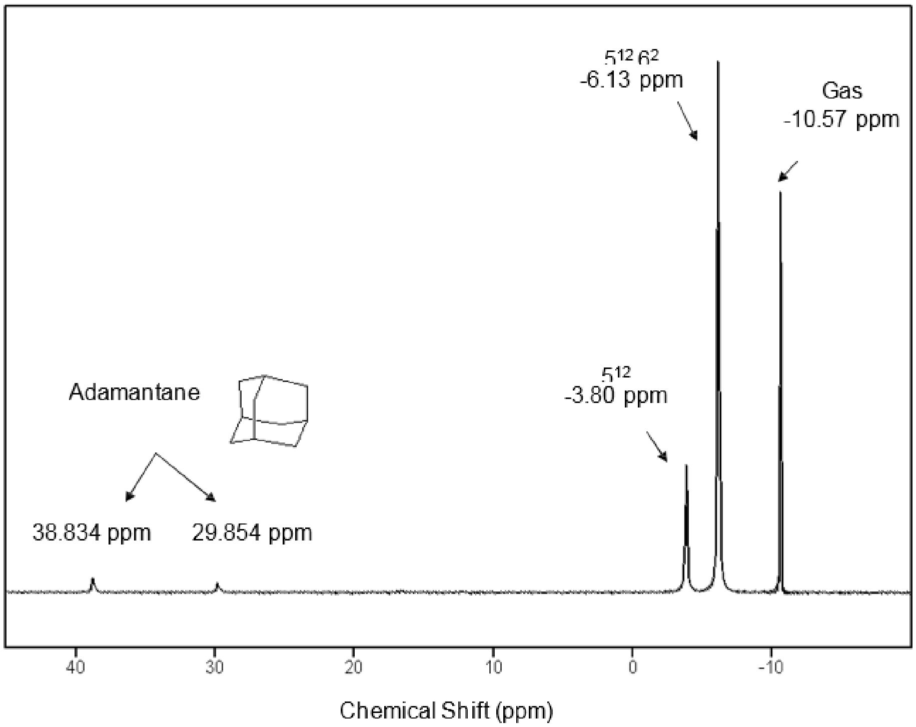

Figure 3. 13C methane hydrate NMR spectrum at 253 K.

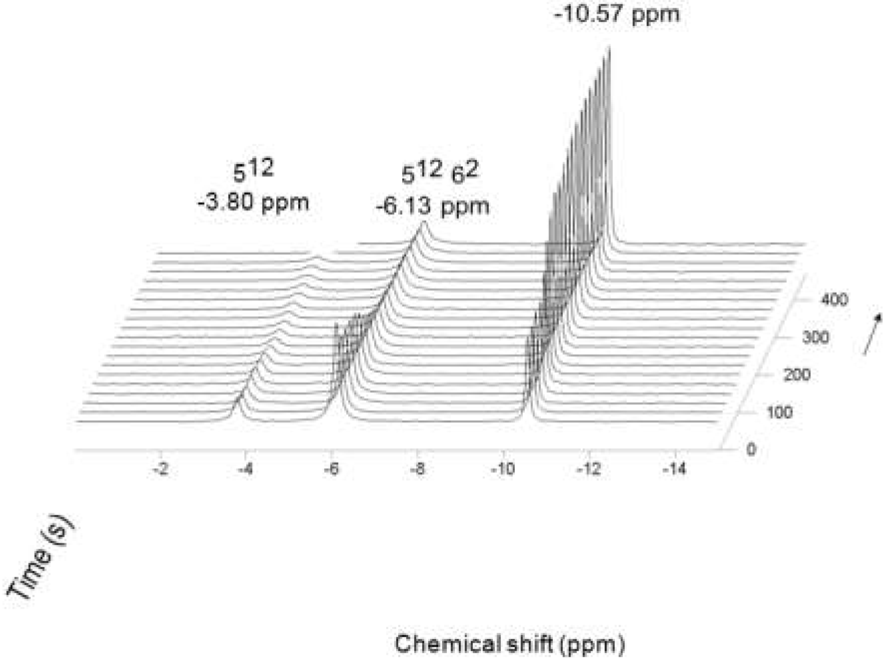

Figure 4. 100.5 MHz time-resolved 13C MAS NMR of sI methane hydrate dissociation during the temperature ramp from 269 K to 271 K. Time-resolution was 5.2048s but only every fifth spectrum is plotted here.

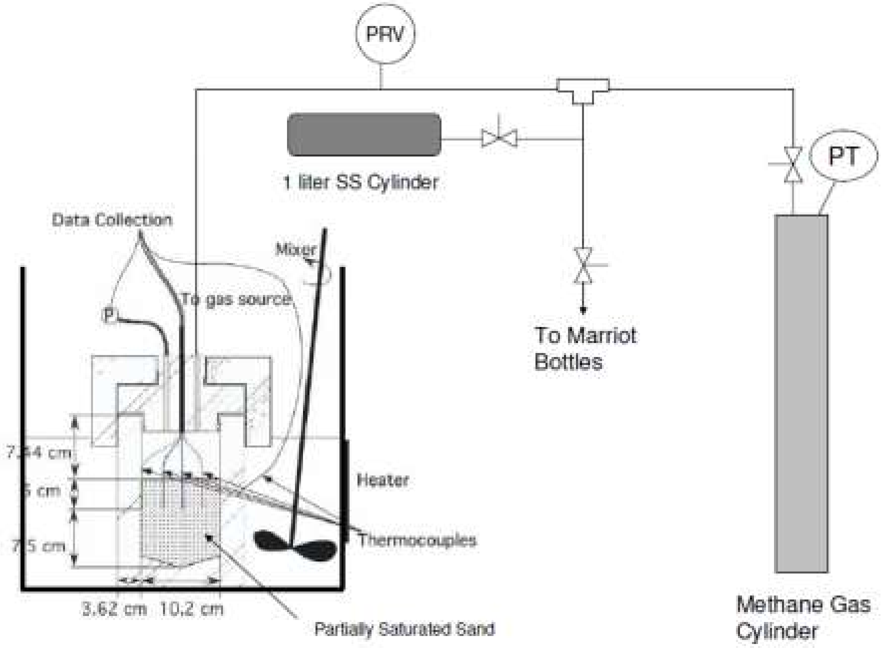

Figure 5. Pressure vessel and experimental setup.

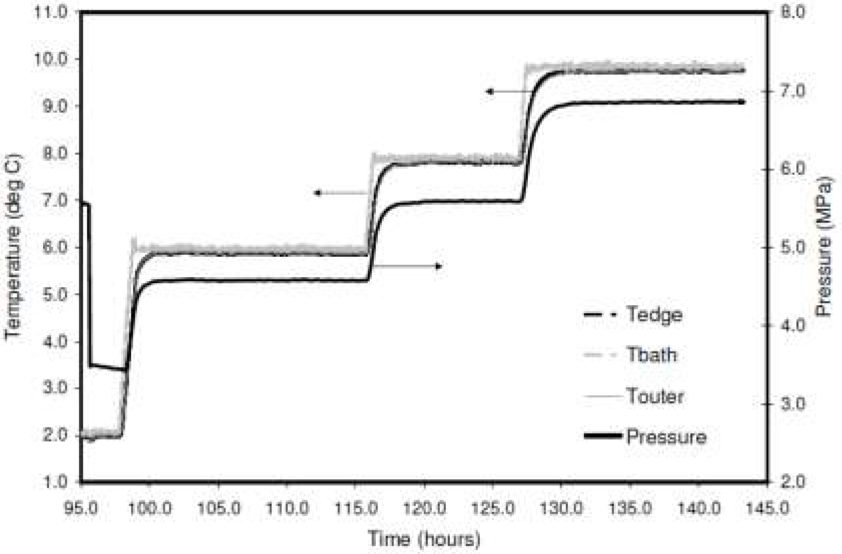

Figure 6. Pressure and temperature during temperature induced hydrate dissociation.

2.3 Comparison of Well Log Data to Ultrasonic Velocities and Attenuation

As we reported in the last reports, we investigated the ultrasonic attenuation of pure THF hydrates. To employ our previous finding we started to use our developed methods on well log data. The well log data was provided by Dr. Guerin from the JIP Gulf of Mexico gas hydrate research wells. In this report, we present our preliminary results from well GC955H. Initial analysis of the data shows the presence of hydrates. A drastic increase in velocities accompanied with a weaker signal can be seen in Figure 7. Blanking is usually observed right above the BSR in a zone where hydrates are present. This blanking is thought to be caused by an impedance factor close to zero which is caused by the presence of hydrates (Lee et all, 2009). Additionally, it has been observed that attenuation increases in the presence of hydrates. We started to perform an analysis of the waveforms by looking at the frequency shift due to attenuation (Figure 8). Four waveforms were chosen: one right above the hydrate bearing layer, two within the hydrate zone and one below the hydrate zone. It can be seen that the frequency content reducer within the hydrate layer. Also, the frequency contents increase in the waveform below the hydrate bearing zone, but it is still lower than the one right above the hydrate zone. This could be explained by the presence of free gas which could cause a higher attenuation. In the next quarter we are going to continue to work on this data set and a data set from the north slope of Alaska to see if there is a correlation between the low frequency and the ultrasonic measurements.

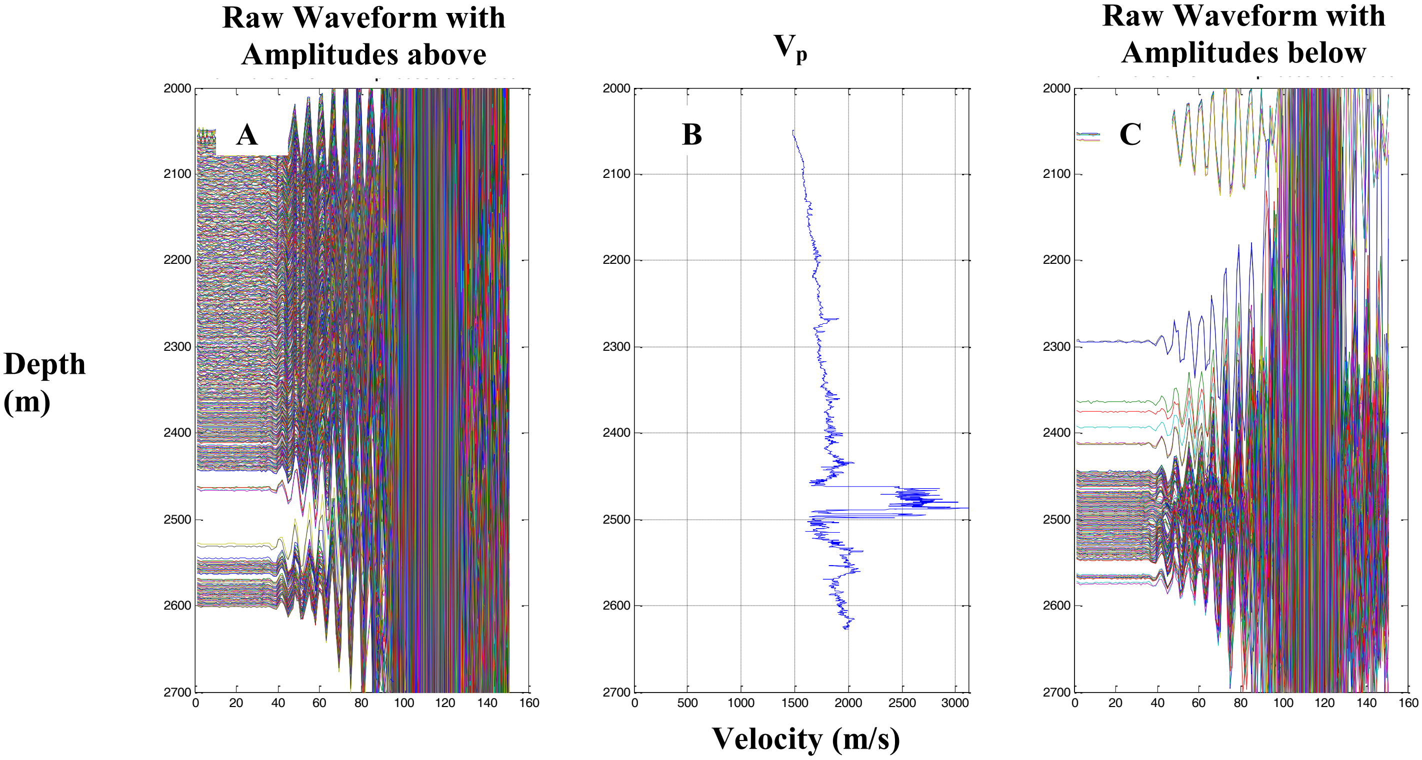

Figure 7. Raw waveform from well log data. (A) shows waveforms with amplitude values of above a 1000 and (C) shows the waveforms with amplitude values below a 1000. As it can be seen the waveforms with lower amplitude values show a correlation with the increase in velocities (B).

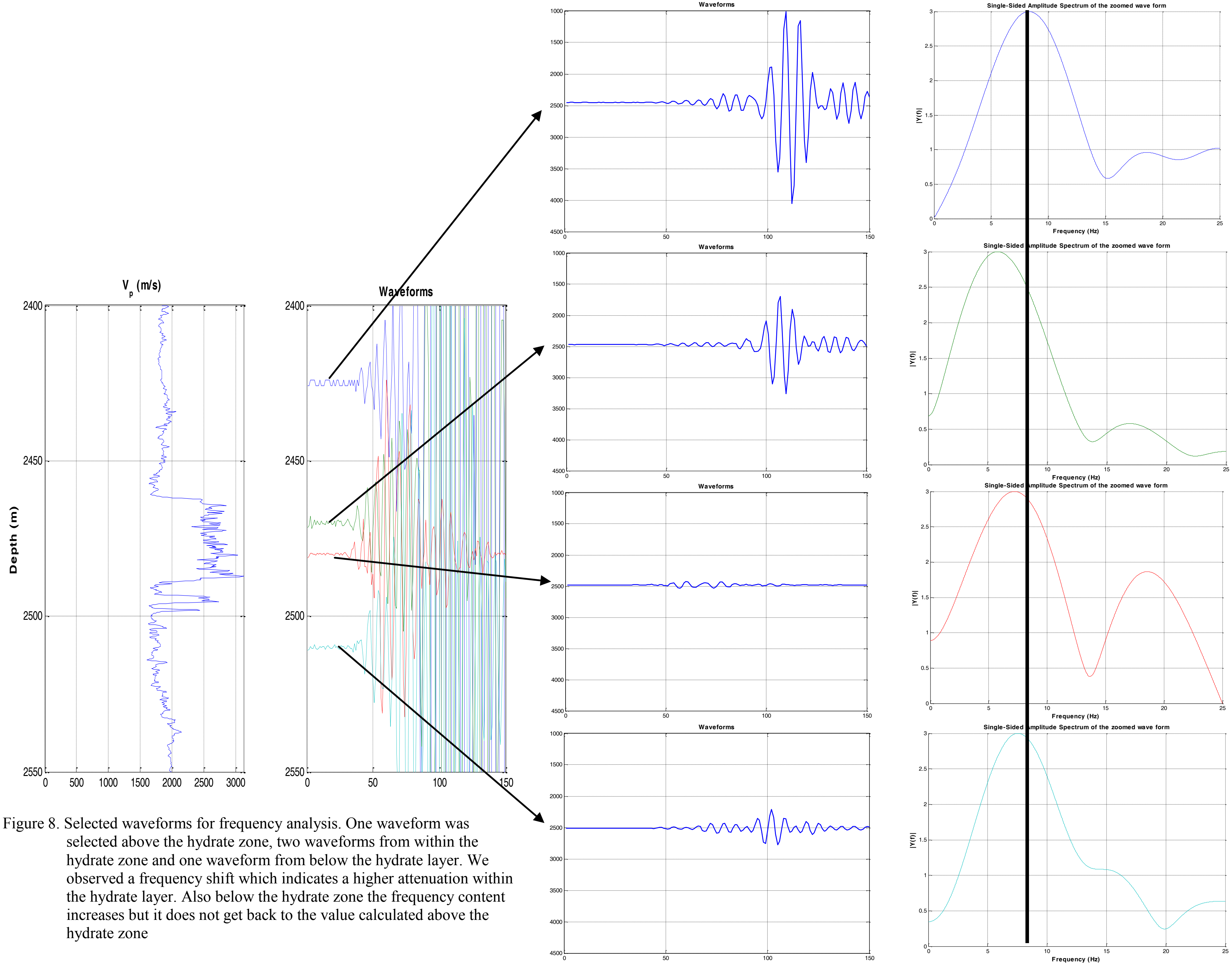

Figure 8. Selected waveforms for frequency analysis. One waveform was selected above the hydrate zone, two waveforms from within the hydrate zone and one waveform from below the hydrate layer. We observed a frequency shift which indicates a higher attenuation within the hydrate layer. Also below the hydrate zone the frequency content increases but it does not get back to the value calculated above the hydrate zone

2.4 Combining MXCT Imaging with Ultrasonic Velocity Measurements

We continued our work towards the simultaneous acquisition of MXCT images and ultrasonic velocities on hydrate-bearing sediments. We build ultrasonic transducers that fit into the torlon pressure vessel introduced in quarterly report Q5 (Figure 9). The transducers consist of piezoelectric PZT P-wave crystals and cylindrical pieces of torlon. Both are connected with conductive epoxy. On the edges and the outward facing side of each PZT crystal (facing away from the sample) we applied a rounded layer of K20 epoxy to avoid the reflection of waves from this direction. The ground wires are attached to the torlon buffer rod and the signal wire is attached to the PZT crystal. The PZT crystals are squares with the dimensions of 2.5 mm by 2.5 mm. This very small size was necessary to fit the transducers into the pressure vessel (inner diameter: 8 mm) while still being able to lead all four wires past the upper transducers.

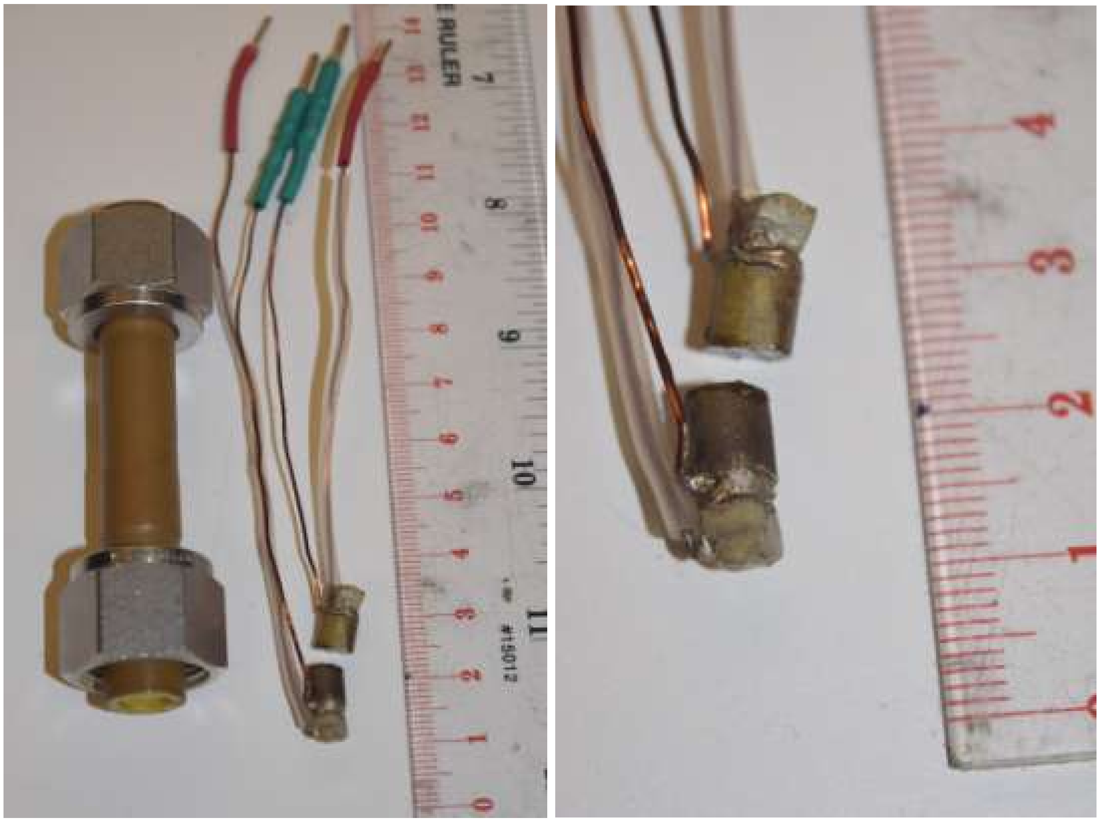

Figure 9. Ultrasonic P-wave transducers and torlon pressure vessel for use in MXCT scanner

We have not planned to use confining pressure in this setup. The lack of confining pressure and the very small dimensions of the transducers led us to the decision to include only P-wave crystals and no S-wave crystals. The S-wave signal that could be acquired under the described conditions would not be useable. However, we are working on two larger pressure vessels (inner diameter: 12 mm) that could allow the collection of P-wave and S-wave data (Chapter 2.5, Figure 13).

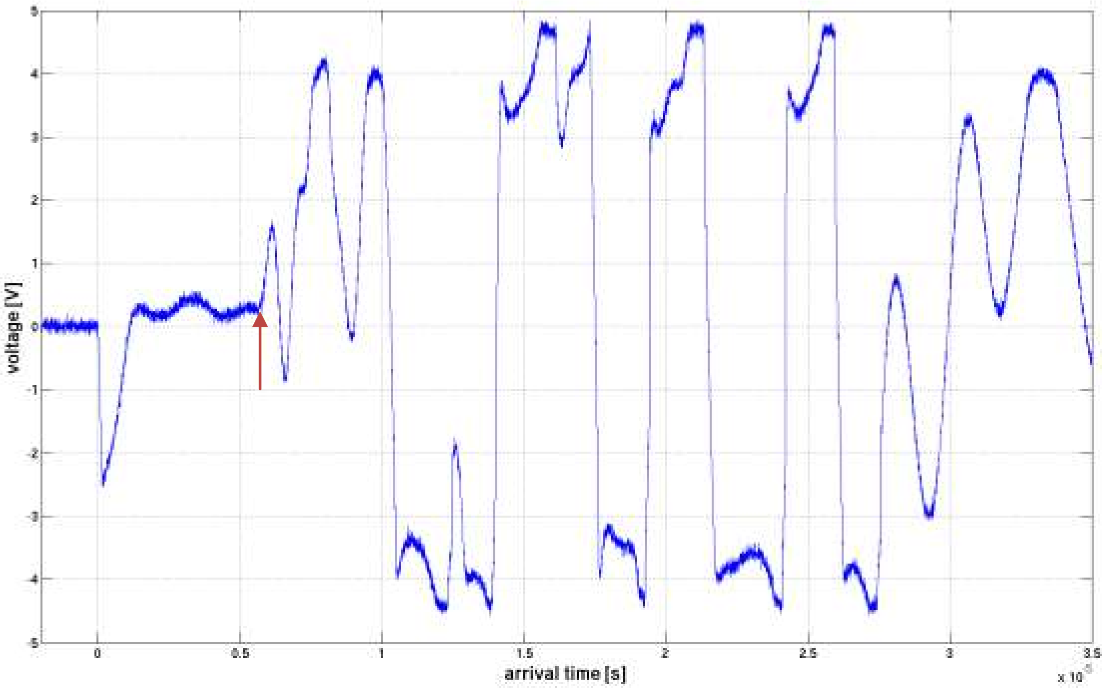

Figure 10. Waveform (P-wave) collected with transducers without sample for dead time estimation, the red arrow indicates time of first arrival

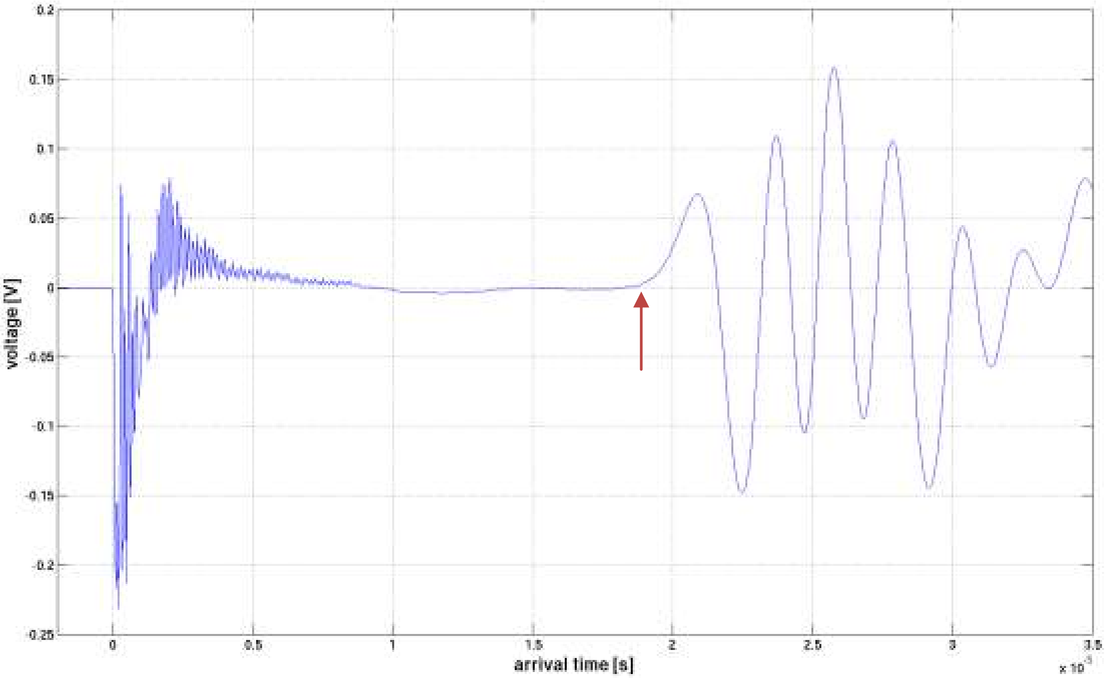

Figure 11. Waveform (P-wave) collected for 22 mm long Bentheim sandstone sample, the red arrow indicates time of first arrival

Example compressional waveforms collected with the transducers are shown in Figures 10 and 11. Figure 10 shows the dead time at atmospheric pressure and T=22.0°C. Figure 11 shows the travel time across a 22 mm long piece of Bentheim Sandstone.

The dead time was estimated as $\boldsymbol{t_d = 5.641 \cdot 10^{-6} s}$, the travel time through the sandstone sample was $\boldsymbol{t = 1.868 \cdot 10^{-5} s}$, resulting in a velocity of $\boldsymbol{v_p = 1687.2\ {}^{m}/_{s}}$.

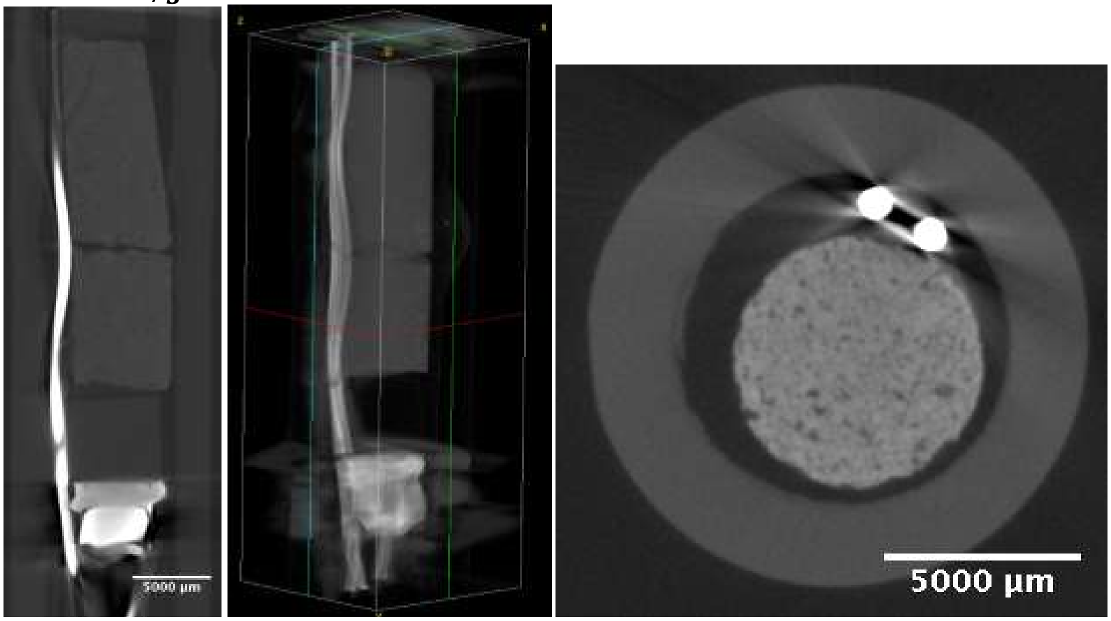

Figure 12 Micro X-ray CT image of transducers with Bentheim sandstone sample inside torlon pressure vessel a) vertical 2D slice b) 3D view c) horizontal 2D slice

Figure 12 shows MXCT images of the transducers with a Bentheim Sandstone sample in the torlon pressure vessel. Only the lower transducer is shown entirely. The torlon buffer of the upper transducer is pictured partially. The PZT crystal, wires and conductive epoxy appear white in the images due to their high density. This high density also causes artefacts in the immediate vicinity of these objects, however, Figure 12 c shows that the sandstone sample itself is not affected by these artefacts. All three images, especially the 3D view, also depict the comparatively low X-ray attenuation caused by the torlon pieces (the vessel and the buffers) prooving that torlon is a suitable material to be used in the MXCT scanner. It should be noted though that the hole in this torlon pressure vessel had to be widened from 6 mm to 8 mm in order to fit the transducers. It will thus not be pressurized in the MXCT scanner but will be used at atmospheric pressure until the manufacturing of the two larger vessels (Chapter 2.5) is completed.

2.5 Preparation of Pressure Vessel for Use in MXCT scanner and NMR machine

As introduced in Chapter 2.2 before, we are working on linking the high field NMR work performed by Arvind Gupta to our work with the low field NMR and the micro X-ray CT. We are currently working on two more torlon pressure vessels to be used in both machines. The vessel shown in Figure 13 has an outer diameter of 27 mm and an inner diameter of 11 mm. A second vessel with outer diameter 52 mm and inner diameter of 20 mm is planned. In Figures 13 and 14 the pressure vessel is filled with F-110 Ottawa Sand for testing. Image 13 shows that we are able to scan through a 8 mm thick wall of torlon without loosing too much of the signal to attenuation. The scanning time for Figure 13 was 100 minutes (magnification: 0.5X, resolution: 53.0 µm). Figure 14 shows a higher resolution scan (magnification: 4X, resolution: 4.61 µm) which was obtained in 10 hours. The greater diameter of this pressure vessel compared to the small one described in Chapter 2.4 causes a notable increase in scanning time (comparable scan in smaller vessel: 6 hours). F-110 Ottawa Sand is a fine sand with an average grain size of 110 µm. For future imaging experiments we will primarily use glass beads with a diameter of 1 mm and industrial quartz sand with a grain size of 400 µm. For these host sediments a lower resolution will be sufficient which would reduce the scanning time. The larger inner diameter allows the use of bigger transducers (better ultrasonic signal quality). The greater wall thickness of this vessel ensures safe use of the vessel under elevated pressure.

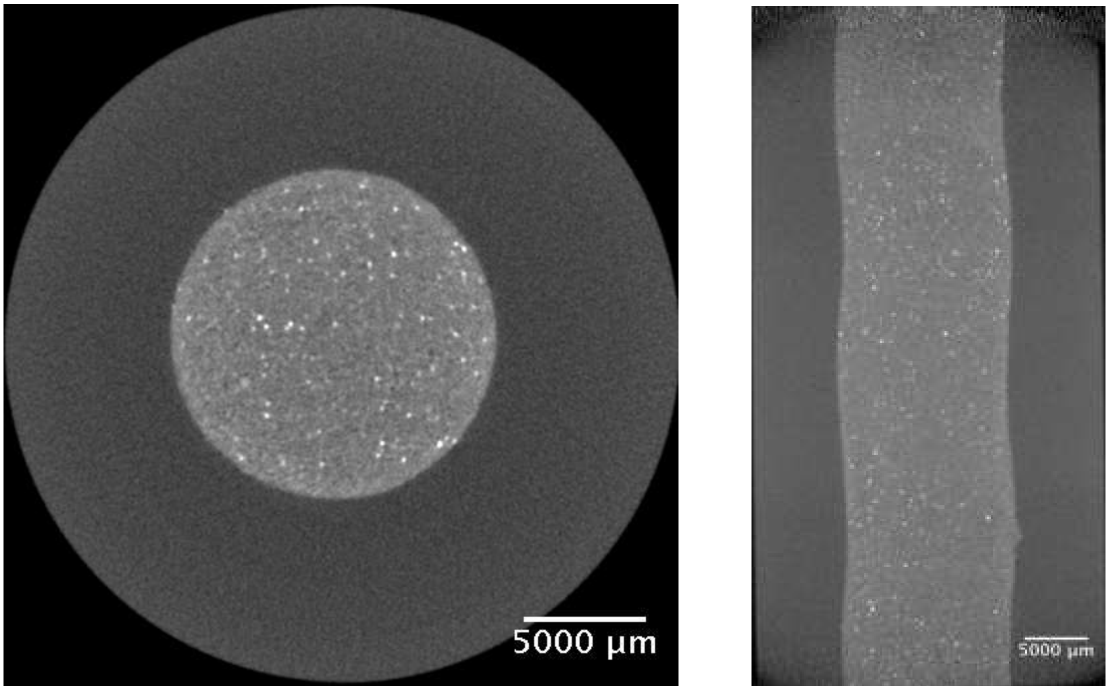

Figure 13. Micro X-ray CT images for CT-NMR torlon pressure vessel (inner diameter: 11 mm, outer diameter: 27 mm) filled with F-110 Ottawa Sand. Image resolution: 53 µm

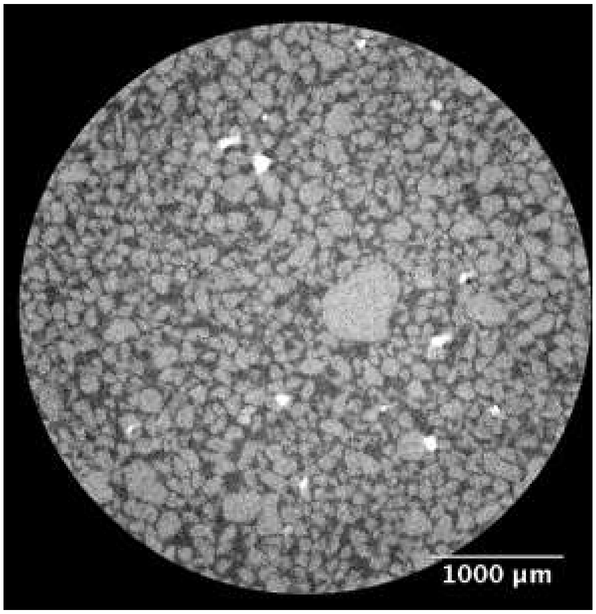

Figure 14. Higher resolution image of F-110 Ottawa Sand taken in CT-NMR torlon-vessel. The field of view here is 4mm wide and does thus only show the central part of the sand sample inside the pressure vessel. Image resolution: 4.61 µm

Reference

Lee, M.W., T. S.Collett, and T. L. Inks, (2009): “Seismic-attribute analysis for gas-hydrate and free-gas prospects on the North Slope of Alaska.” in T. S. Collett, A. Johnson, C. Knapp, and R. Boswell, eds., Natural gas hydrates—Energy resource potential and associated geologic hazards. AAPG Memoir 89, p. 541–554.

Gupta, A. (2007): ”Methane Hydrate Dissociation Measurements and Modeling: The Role of Heat Transfer and Reaction Kinetics.“, Ph.D. Thesis, Colorado School of Mines, Department of Chemical Engineering

3. Acknowledgments

We thank the US Department of Energy for sponsoring the project. We also thank Tim Collett for his cooperation with us on this project. We acknowledge support of some personnel by other grants (DHI/Fluids and OCLASSH consortia, Chinese Mining University).

4. Plans

We plan to focus on CH_4 hydrates in acoustics, low frequency measurements and MXCT scanning. For that purpose we will collaborate with the Center for Hydrate Research in the Department of Chemical Engineering at Colorado School of Mines to make use of their expertise with methane hydrates. We will continue our work on NMR measurements of hydrate-bearing sediments and work on a cooling system for the NMR machine. The newly developed ability to obtain ultrasonic data during MXCT imaging will be applied to hydrate-bearing sediments.

Table 2. Q12 Milestones and Deliverables

Milestone	Task	Description	Completion date	Report Content
7	6	Methane hydrates from free gas phase	12/31/2015	Progress report
10	9	NMR/MXCT characterization	9/30/2015	Progress report
12	11	Comparison to log data	12/31/2015	Progress report
13	12	Information dissemination	12/31/2015	Progress report

5. Products

Publications (Publications; Conference Papers, Presentations, Books)

Conference presentations and expanded abstracts at 3IWRP (3rd International Workshop on Rock Physics) in Perth, Western Australia, April 2015

Pohl, M. and Batzle, M.: "Ultrasonic Attenuation of Pure THF-Hydrate"

Schindler, M., Batzle, M. and Prasad, M.: "Pore-Scale Imaging and Ultrasonic Velocity Measurements of Hydrate Bearing Porous Media"

Presentation slides and expanded abstracts are attached as separate files. Please note that Mandy Schindler originally submitted an abstract with a different topic (covered in quarterly report Q8) and changed the title of her presentation.

Website or other Internet sites
http://crusher.mines.edu/CRA-DOE-Hydrates

Technologies or techniques
Nothing to report

Inventions, patent applications and/or licenses
Nothing to report

Other Products
Nothing to report

6. Participants and Collaborating Organizations

CSM personnel:

Name:	**Manika Prasad**
Project Role:	Principle Investigator
Nearest person month worked this period:	0.25
Contribution to Project:	Dr. Prasad helped with acoustic and attenuation measurements
Additional Funding Support:	Academic faculty
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),	N/A
Duration of stay:	N/A

Name:	**Michael Batzle**
Project Role:	Principle Investigator
Nearest person month worked this period:	0
Contribution to Project:	Dr. Batzle was responsible for the overall (dis)organization of the project.
Additional Funding Support:	Academic faculty
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),	N/A
Duration of stay:	N/A

Name:	**George Radziszewski**
Project Role:	Research Faculty
Nearest person month worked this period:	0
Contribution to Project:	Dr. Radziszewski spent his time establishing standards and procedures for running the MXCT scanner but is now retired.
Additional Funding Support:	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),	N/A
Duration of stay:	N/A

Name:	**Weiping Wang**
Project Role:	Laboratory Manager

Nearest person month worked this period:	1
Contribution to Project:	Mr. Wang assisted in equipment fabrication
Additional Funding Support:	DHI/Fluids consortium, Chinese Mining University
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):	China
duration of stay: N/A:	2 weeks

Name:	**Mathias Pohl**
Project Role:	Ph.D. 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:	Yes
If traveled to foreign country(ies)	Australia
duration of stay:	2 weeks

Name:	**Mandy Schindler**
Project Role:	Ph.D. 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:	Yes
If traveled to foreign country(ies),	Australia
duration of stay:	1 week

Name:	**Hanna Flamme**
Project Role:	Student
Nearest person month worked:	1
Contribution to Project:	Ms. Flamme assisted with equipment testing and data collection.
Additional Funding Support:	DHI/Fluids Consortium
Collaborated with individual in foreign country:	No
Country(ies) of foreign collaborator:	N/A
Travelled to foreign country:	No
If traveled to foreign	N/A

country(ies):	
duration of stay:	N/A

Name:	**Andrew Markley**
Project Role:	Student
Nearest person month worked:	0.5
Contribution to Project:	Mr. Markley assisted with data collection and is responsible for the website.
Additional Funding Support:	DHI/Fluids 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):	N/A
duration of stay:	N/A

External Collaborations:

Dr. Tim Collett
US Geologic Survey
Denver, Colorado

Support: Dr. Collett provided data and guidance on interpretation and application. He continues to publish numerous papers on hydrate properties.

7. Changes / Problems

Several factors will occur that might impact the progress of this project.
George Radziszewski is retired as of April 30, 2015. He has been responsible for much of the CT imaging conducted on our hydrate-bearing sediments. Mandy Schindler has been training Weiping Wang, our laboratory manager, and student Andrew Markley to perform some of the tasks. The MXCT imaging is now performed by the three of them.

Mathias Pohl will be spending 6 weeks during quarter Q12 perfoming low frequency velocity and attenuation measurements at NTNU Trondheim, Norway under the guidance of Rune Holt.

8. Special Reporting Requirements

None

9. Budgetary Information

Attached separately