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Quarterly Research Performance Progress Report (Period ending 12/31/2014)

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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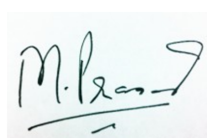

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Abstract

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

Grant/Cooperative Agreement DE-FE 0009963.

During this period we modified the setup in the MXCT scanner to allow cooling for extended periods of time. This is a step towards the formation of methane hydrate in the MXCT scanner. As a proof-of-concept, MXCT images were recorded for THF-hydrate bearing glass bead packs.
In addition, ultrasonic measurements of THF-hydrate bearing sand packs were performed to investigate the influence of confining pressure on ultrasonic attenuation.

- Attenuation in THF-hydrate bearing clean quartz sand packs decreases with increased confining pressure

- THF hydrate forms homogeneously (no hydrate clumps) on the small scale observable in the MXCT scanner

- THF hydrate fills the pore bodies of glass-bead pack and has contact with the surfaces of the glass beads

- Barium chloride brine fills smaller pores and is found at the surfaces of glass beads

- THF hydrate can be distinguished from glass beads and barium chloride brine in MXCT images based on gray scale value

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2. Accomplishments

2.1 Overview of Milestone Status

Our current position is shown in the time chart in Figure 1 and the Milestone status is shown in Table 1. In the current period of Q9 (Q1 of Year 3), we continued our work on Task 9 – MXCT Characterization and Task 5 – THF Hydrate-Bearing Rock. The two students working on this project, Mandy Schindler and Mathias Pohl are preparing to defend their second comprehensive exam (thesis proposal). Mathias will defend his proposal in Q10 and Mandy in Q11.

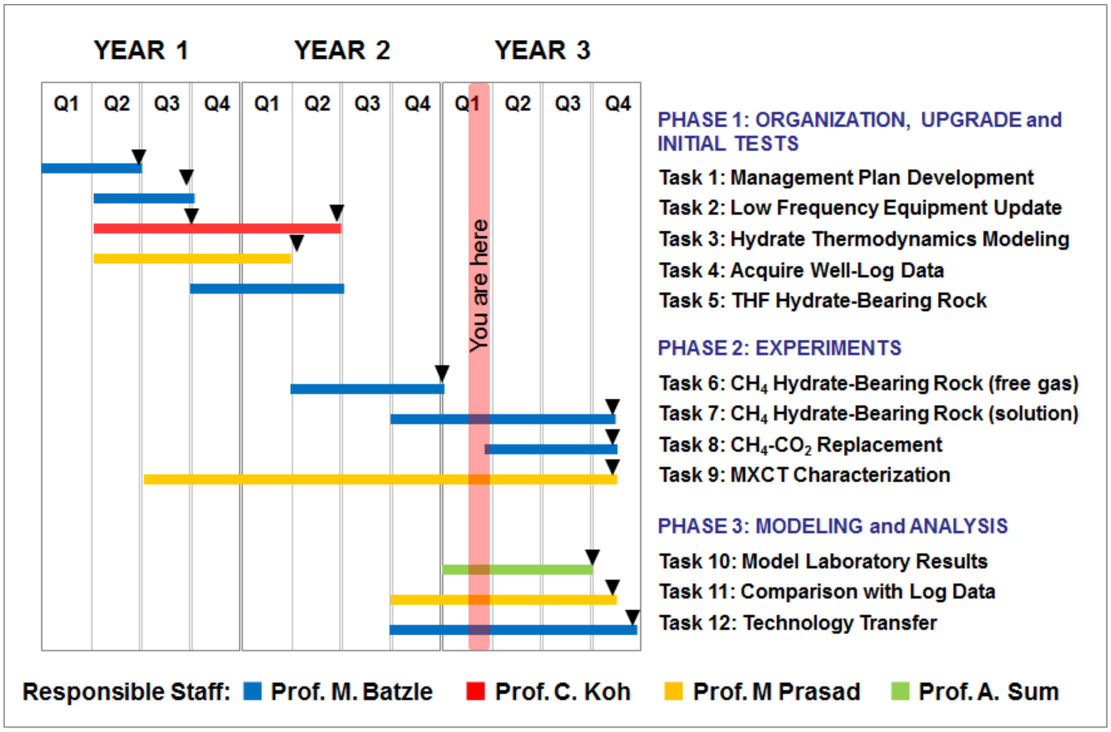

Figure 1. Milestone Status. We are at the end of our nineth quarter and are approaching the start of the final phase of this project.

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*	30 June 2015
Continuing or Planned			
8	Methane hydrates from gas in solution	Planned	30 Jun 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 Ultrasonic Attenuation Measurements of THF Hydrate-Bearing Sand Packs

As described in the previous report we can determine attenuation from ultrasonic waveform measurements by using the spectral ratio method. Measurements have been performed on sand packages containing pure Ottawa Sand F110 which is pure Quartz sand. Furthermore, 10 and 30 wt% of Kaolinite were mixed into the sand to investigate the influence of clay on ultrasonic velocities and attenuation. Figure 2 shows the P- and S-wave velocities measured in Sample 19 for each measurement step.

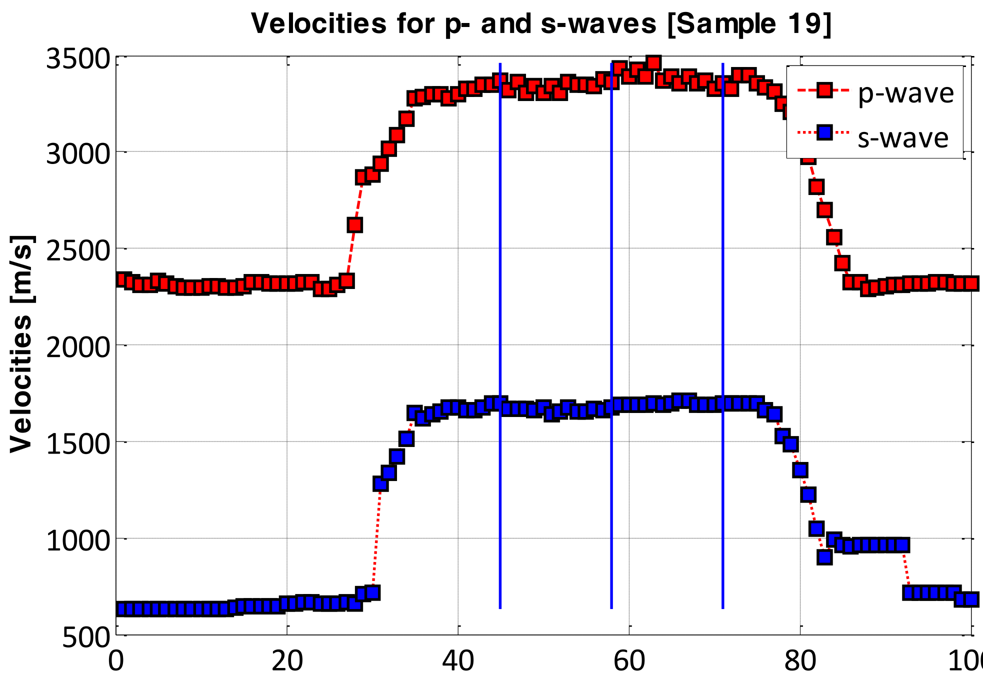

Figure 2. Shows all the calculated velocities for Sample 19. X-axis gives the successive measurement points.

Three sets of measurements were conducted for each sample - first the cooling, second a pressure cycle, and third the heating of the sample. During the cooling, the temperature was lowered so that it was suitable for hydrate formation. During the pressure cycle, the differential pressure of the sample was raised up to 2200 psi and then lowered back to 435 psi. The heating of the sample caused the dissociation of the hydrates. Figure 2 shows the calculated velocities for Sample 19. It can be seen that during the pressure cycle (between measurement points ca. 40 to about 75), the velocities stay the same. This can be explained by the fact that this specific sample had 30 %wt clay and also a low porosity (around 10 %). Additionally, the increase in velocity with hydrate formation (around measurement point 30) indicates that the hydrates are load bearing and cause the sand sample to become stiffer.

Preliminary results have been obtained for the attenuation in these samples. Figure 3 shows the first p-wave arrival for the first part of the pressure cycle (increasing pressure). As it can be seen, the waveforms shift to faster arrival times indicating a faster p-wave velocity. This pressure cycle was taken from a sample containing only quartz. Figure 4 shows the frequency spectra for the waveforms shown in Figure 3. In theory, one would expect a reduction in attenuation when the pressure increases. This can be observed in Figure 4. With increasing pressure we can see that the spectra contain more information in the higher frequencies. Nevertheless this increase in frequency content is relatively small indicating that the attenuation decreases only by a little bit with increasing pressure.

In the future it is planned to evaluate all of the data sets in regard of their p- and s-wave attenuation and to determine the influence of clay.

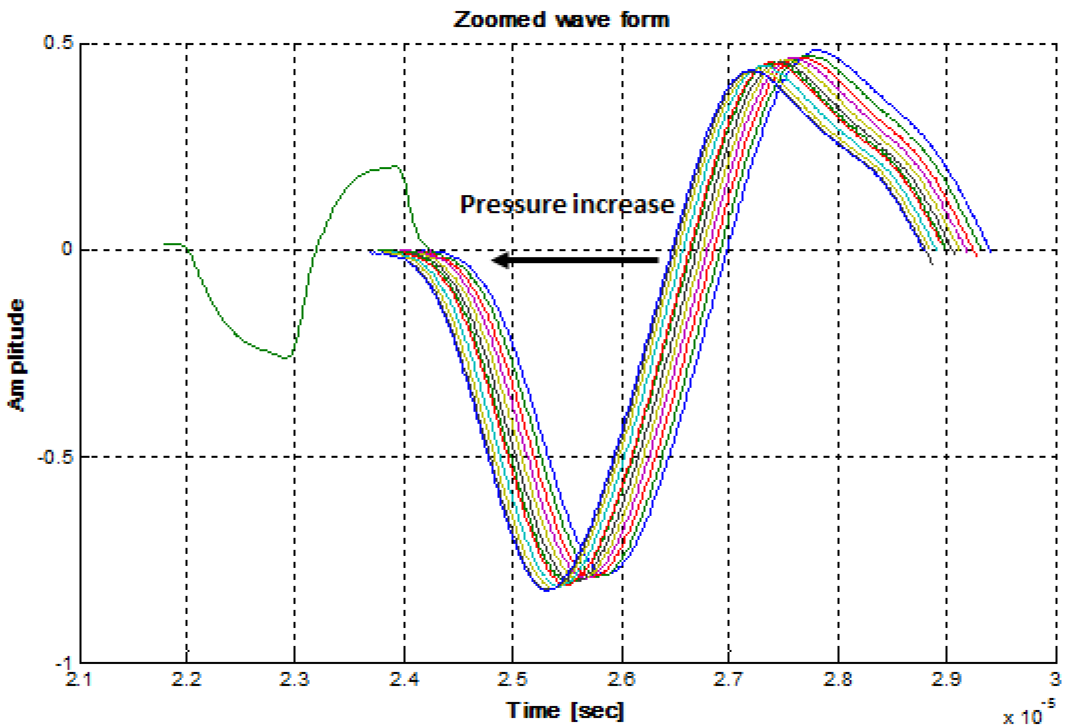

Figure 3. Frequency content of the recorded p-waves during the pressure cycle. As it can be seen, the frequency content increases as the pressure is increased.

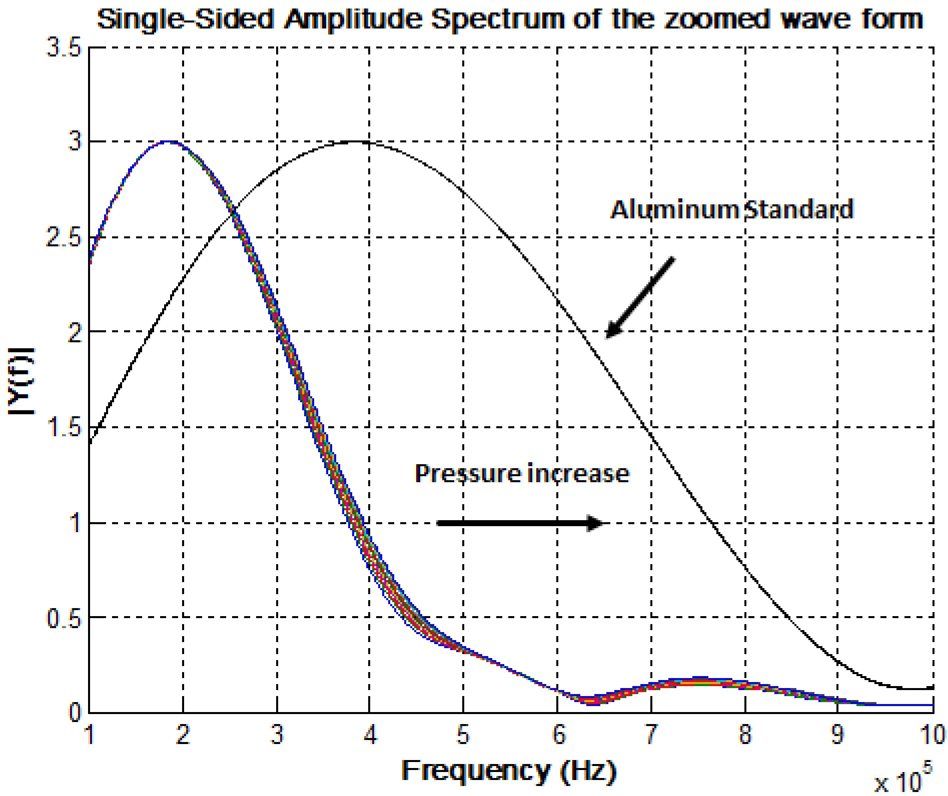

Figure 4. Change in waveforms with increasing confining pressure for a 100 % Ottawa Sand sample containing 80 % THF hydrate in the pore space. The pressure was increased from 435 psi to 2175 psi causing a shift to the left of the waveform resulting in an increase in velocity. The green waveform on the left is the reference waveform.

2.3 Preparation of MXCT Scanner for CH_4 Experiments

The cooling system in the MXCT scanner is now functional and has been tested on THF-hydrate bearing glass-bead packs. Air from a compressor is led through a copper coil in a temperature bath filled with ethylene glycol with a temperature of approximately -30°C. The cooled air is then used to cool the sample inside the CT scanner. Modifications made to ensure sufficient cooling were:

1. We are using compressed air instead of compressed nitrogen now to be able to cool for longer periods of time without having to change the gas cylinder.
2. The air hose is now paired with a hose loop flowing cooled ethylene glycol. Both hoses are insulated until they reach the sample.
3. The pressure cell containing the sample is covered with a plastic cylinder to confine to cooled air to a small volume around the pressure cell.

We managed to cool the sample with this method to approximately 2°C. This temperature is sufficient to form THF hydrates at atmospheric pressure and methane hydrate at a pressure of 8 MPa without forming ice. The pressure cell has been tested for pressures up to 34.5 MPa.

To test the functionality of the cooling system, we formed THF hydrate in a glass-bead pack and recorded MXCT images shown in Figures 5 - 7. The temperature was kept stable for more than 30 hours.

For previous experiments, we had formed THF hydrate outside of the MXCT scanner and used dry ice for temporary cooling during the scanning process (approximately 2 hours). The longer period of stable, low temperatures allows MXCT scans at higher resolution and of better image quality (Figures 6 and 7). Stable temperatures below 4°C are necessary for the formation of CH4 hydrates which is planned for period Q10.

Figure 5 shows MXCT images taken at lower resolution to cover a large portion of the sample. At this scale, we observe no discrete hydrate bodies but hydrate disseminated throughout the pore space rather homogeneously. The barium chloride brine seems to fill smaller pores.

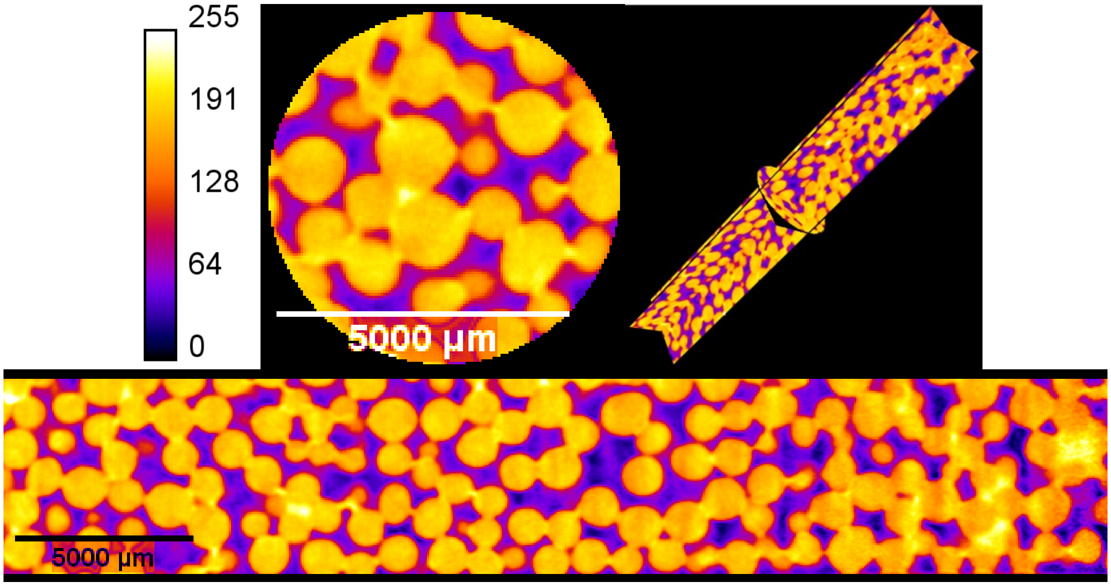

Figure 5. MXCT images of THF-hydrate bearing glass-bead pack at low resolution (1 pixel = 45.4 µm). Filename: CT_vessel_GB_THF_5. Violet: THF hydrate, light yellow: $BaCl_2$ brine, yellow/orange: glass beads.

Figure 6 and Figure 7 show high resolution MXCT images. We observed that barium chloride brine is located in small pores and along the grain surfaces while THF hydrate fills larger pore bodies. THF hydrate seems to have contact with the glass bead surfaces.

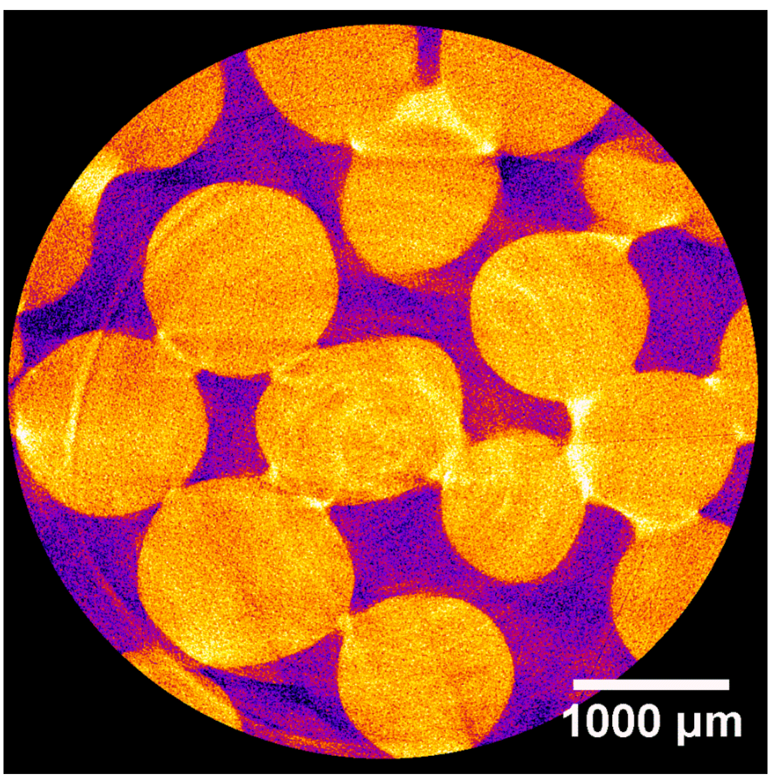

Figure 6. MXCT image at 4X resolution (1 pixel = 5 µm). Filename: CT_vessel_GB_THF_9. Violet: THF hydrate, light yellow: $BaCl_2$ brine, yellow/orange: glass beads.

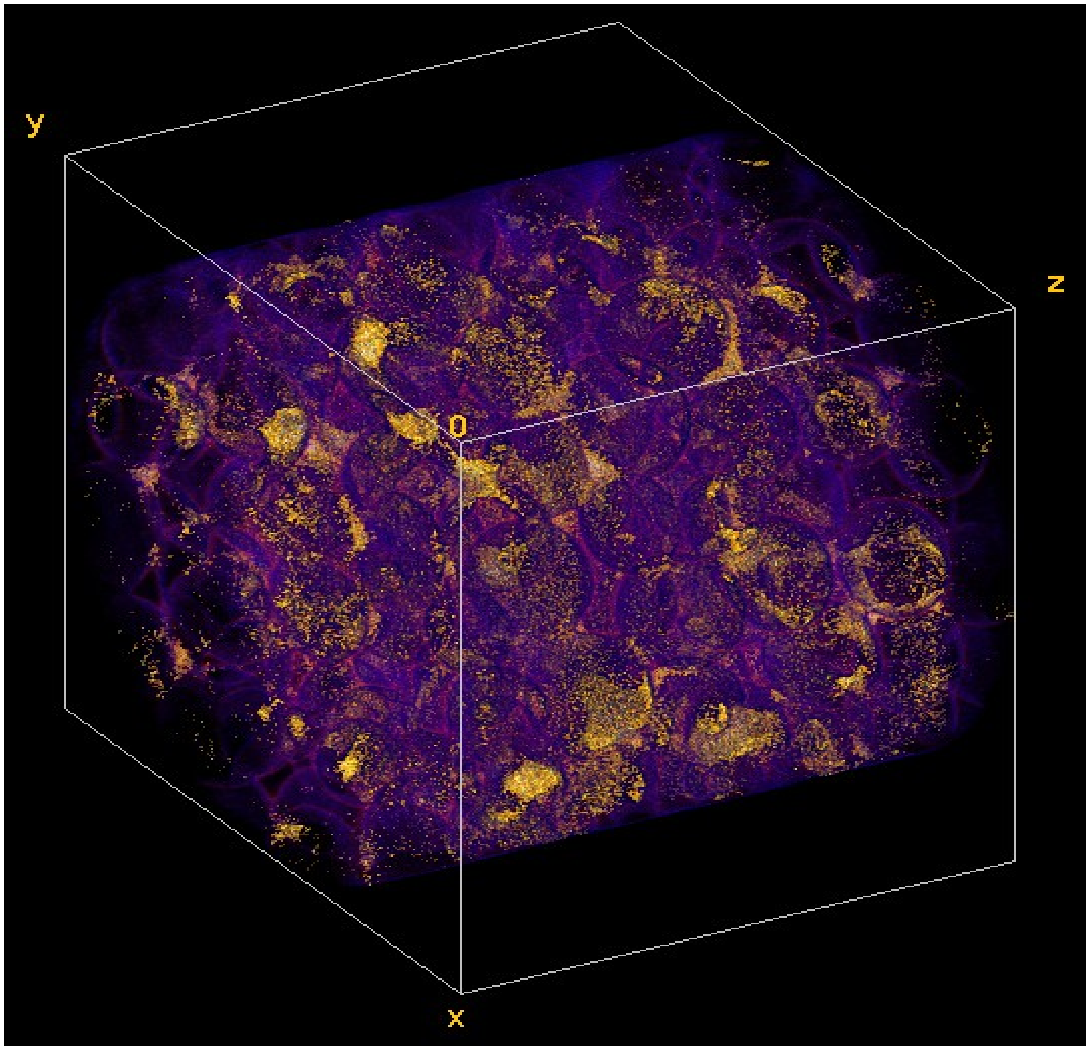

Figure 7. 3D reconstruction of a stack of tomographic images. Filename: CT_vessel_GB_THF_4. Glass beads have been cut out, $BaCl_2$ brine is shown in yellow and THF hydrate in violet.

Figure 8 shows a histogram for the three sample components: THF hydrate, glass beads and barium chloride brine. The gray values for THF hydrate and glass beads form two separate Gaussian distributions with little overlap. A smaller Gaussian distribution at the highest gray scale values represents areas filled with barium chloride brine. The overlap in gray scale for glass beads and barium chloride brine makes the distinction of these two components problematic. However, THF hydrate can be clearly distinguished from barium chloride brine and glass beads. The gray value distributions for each phase in the sample can be used to identify different materials in further MXCT images based on their gray value. Figure 9 shows the histogram of a stack of 600 MXCT images. The histogram shows the two distinct peaks for THF hydrate and glass bead. Barium chloride brine does not appear as a separate peak though due to a smaller area (lower pixel count) filled with barium chloride brine.

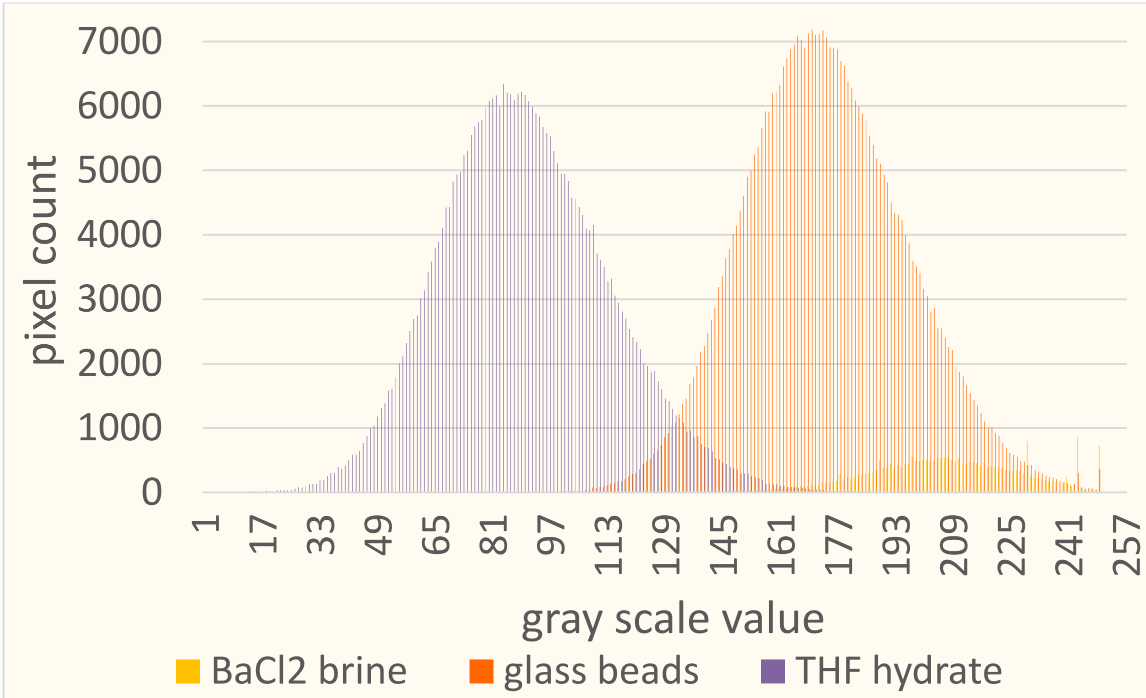

Figure 8. Histogram of representative areas of 3 sample components. THF hydrate and $BaCl_2$ brine can be clearly distinguished based on their gray scale value in tomographic images.

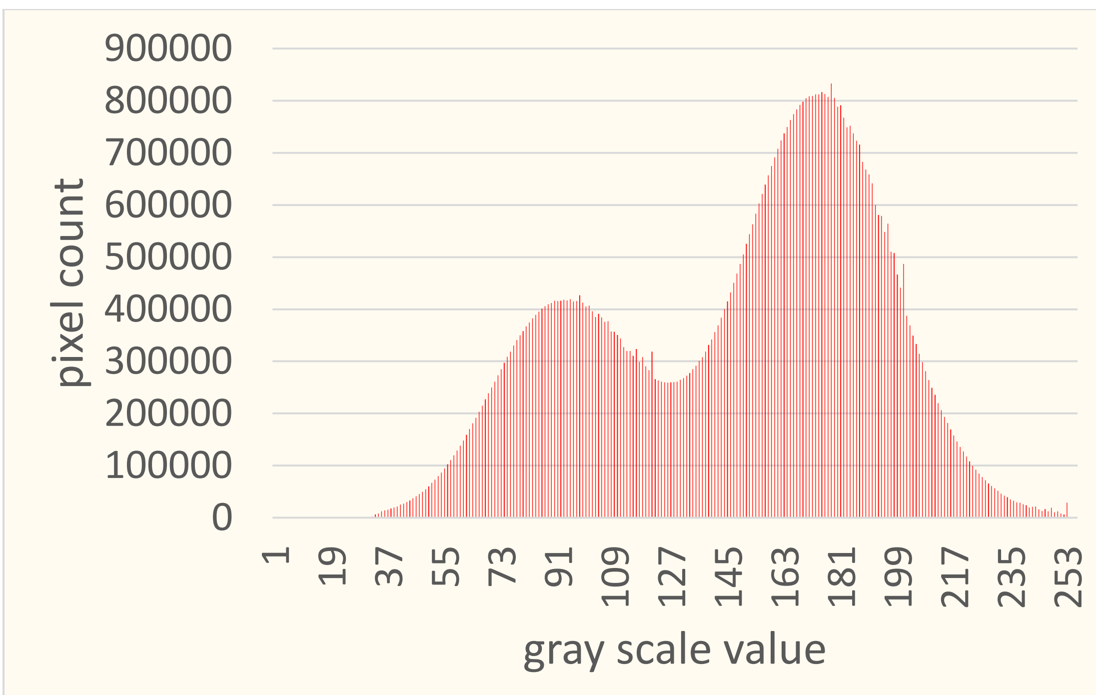

Figure 9. Histogram for entire stack of MXCT images (Filename: CT_vessel_GB_THF_9)

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

Table 2 shows the Milestones and Deliverables for this quarter. We plan to focus on CH4 hydrates in both, low frequency measurements and MXCT scanning. We further plan to include ultrasonic crystals into the MXCT setup to obtain ultrasonic velocity measurements while recording MXCT images. The analysis of the preliminary attenuation data shown in this quarterly report will be finished during the next quarter. We are delayed in Milestone 7. It was scheduled to be completed in this quarter. However, due to various delays in our experimentation and hydrate-forming protocols, we anticipate a more realistic completion date of 6/30/2015.

Table 2. Q10 Milestones and Deliverables

Milestone	Task	Description	Completion date	Report Content
7	6	Methane hydrates from free gas phase (delayed)	6/30/2015	Progress report
10	9	NMR/MXCT characterization	9/30/2015	Progress report
13	12	Information Dissemination	12/31/2015	Progress report

5. Products

Publications (Publications; Conference Papers, Presentations, Books)
Nothing to report

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:	Yes
If traveled to foreign country(ies),	India, Norway, Germany, Houston
Duration of stay:	1 months

Name:	**Michael Batzle**
Project Role:	Principle Investigator
Nearest person month worked this period:	1
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:	1.5
Contribution to Project:	Dr. Radziszewski spent his time establishing standards and procedures for running the MXCT scanner.
Additional Funding Support:	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:	1.5 months

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:	3 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:	No
If traveled to foreign country(ies)	N/A
duration of stay:	N/A

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),	Germany
duration of stay:	4 weeks

Name:	**Hanna Flamme**
Project Role:	Student
Nearest person month worked:	1
Contribution to Project:	Ms. Flamme modified and tested the cooling system for the MXCT scanner.
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

Name:	**Andrew Markley**
Project Role:	Student
Nearest person month worked:	0.5
Contribution to Project:	Mr. Markley will help collect CT data.
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 projects.

The sudden passing of principle investigator Michael Batzle in January 2015 left us without our fearless leader. His presence is missed.

The co-Investigators (Carolyn Koh, Amadeu Sum, and Manika Prasad) agree for Manika Prasad to lead the project since Mike's participation for the remainder of the project is uncertain. The CSM administration will prepare paperwork to have the Principle investigator name changed. George Radziszewski plans to retire by the end of April 2015. He has been responsible for much of the CT imaging conducted on our hydrate-bearing sediments. The plan is to utilize Weiping Wang, our laboratory manager, and students Hanna Flamme and Andrew Markley to perform some of the tasks. Weiping is currently being training while Hanna and Andrew have considerable training in CT-imaging. In addition, George Radziszewski will be working on the project part time starting in March.

We will also need to reconcile the project ending dates: Michael Batzle has been planning on project ending December 31, 2015 (see Table 2); but close inspection of contract gives an ending date of September 31, 2015. We will expect to have a better idea of a realistic project ending date in the coming quarters.

8. Special Reporting Requirements

None

9. Budgetary Information

Attached separately