DOE Award No.: DE-FE-0009963

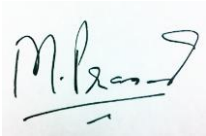
Quarterly Research Performance Progress Report (Period ending 03/31/2016)

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

Project Period (10/1/2012 to 12/31/2016)

Submitted by:
co-PI: Manika Prasad
Colorado School of Mines
DUNS #010628170.
1500 Illinois Street
Golden. CO 80401
e-mail: mprasad@mines.edu
Phone number: (303) 273-3457

Submission Date: 4/30/2016



Prepared for:
United States Department of Energy
National Energy Technology Laboratory

Office of Fossil Energy

Disclaimer

Abstract

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

Grant/Cooperative Agreement DE-FE 0009963.

In this quarter, we concentrated our efforts in building pressure vessels to form methane hydrates while making CT and NMR measurements. Main findings of this study include:

NMR studies: We demonstrate NMR spectra recorded during hydrate dissociation. The collected NMR spectra are constant and consistent when hydrate equilibrium is reached in closed systems. We find that existence of fluid interfaces in partially dissociated hydrate samples in a closed system that are believed to give late time NMR T2 response. The exact cause of this late time response will be investigated in the next quarter

Pressure vessel studies: We developed a pressure vessel and ultrasonic transducers suitable for the use in the micro CT machine. We tested functionality of the pressure and temperature control system and demonstrate that changes in rock samples can be imaged within the resolution constraints of the Xradia-400 machine. We observe compaction of samples subjected to confining pressures resulting in grain damage and fracturing of sediment grains. When the confining pressure was decreased some cracks experienced further fracturing. The grain damage is irreversible. Further fracturing of grains in pre-compacted sediment was observed upon repeated confining pressure cycling.

We included feed-throughs with electrical wires for a pressure vessel which will be used to perform ultrasonic and complex resistivity measurements. This updated setup has been pressure tested. Also, nine samples have been prepared to perform ultrasonic and complex resistivity measurements during hydrate formation.

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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. Note that we have been granted a no-cost extension until December 31, 2016. In the current period of Q14 (Q2 of Year 4), we continued our work on Task 9 – MXCT Characterization. We also updated our equipment to perform higher resolution µCT measurements.

Students: Ms. Schindler successfully defended her second comprehensive exam (thesis proposal).

Publications: The two manuscripts submitted to Geophysical Prospecting have been reviewed and resubmitted.

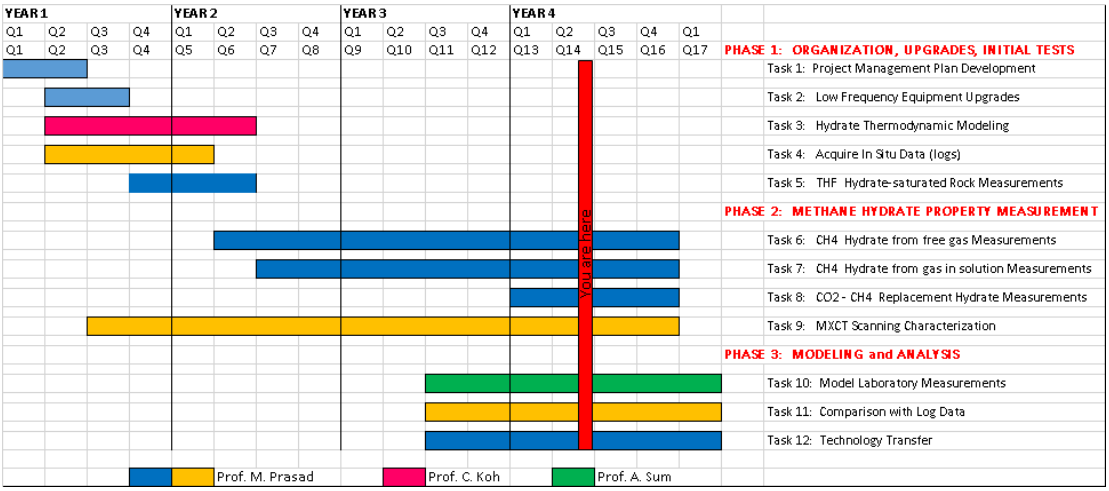

Figure 1: Milestone Status. We are at the end of our 14th quarter and in the final phase of this project. In February 2016, we requested and were granted a no-cost extension until December 31, 2016.

Table 1: Milestone status

Milestone	Title / Description	Status	Date: expected completed or)
Completed			
PHASE 1: ORGANIZATION, UPGRADES, INITIAL TESTS			
Task 1	Project Management Plan Development	Complete & approved	1-Dec-12
Task 2	Low Frequency Equipment Upgrades	Completed	1-Jun-13
Task 3	Hydrate Thermodynamic Modeling	Completed	31-May-14
Task 4	Acquire In Situ Data (logs)	Completed	31-May-14
Task 5	THF Hydrate-saturated Rock measurement	Completed	15-Jun-14
Task 6	THF hydrate grown in pressure vessel	Completed	15-Apr-14
Continuing or Planned			
Task 7	CH4 Hydrate from free gas Measurements	Continuing*	1-Oct-16
Task 8	CH4 hydrate (gas in solution) measurement	Continuing*	31-Oct-16
Task 9	CO2-CH4 replacement hydrate measurement	Planned	30-Nov-16
Task 10	MXCT Scanning Characterization	Continuing*	30-Nov-16
Task 11	Model Laboratory Measurements	Continuing*	30-Nov-16
Task 12	Comparison with Log Data	Planned	30-Nov-16
Task 13	Technology Transfer	Continuing*	31-Dec-16
* initial stages were completed on schedule, but the process continues throughout the project			

2.2 Measurements of Cyclopentane Hydrate Dissociation in NMR

Currently, Nuclear Magnetic Resonance (NMR) is available for classification of fluids in our laboratory. The NMR setup is a low-field 2 MHz Magritek NMR with a magnetic field of 0.05 Tesla. Transverse relaxation (T2) spectra are collected using CPMG sequences. The goal of this work was to record dissociation of a cyclopentane hydrate performed within the NMR in order to test for memory effect of hydrate formation. This was accomplished by first establishing an NMR reading for samples of pure liquid cyclopentane to capture the expected T2 response of these bulk fluids in their dissociated state (Figure 2).

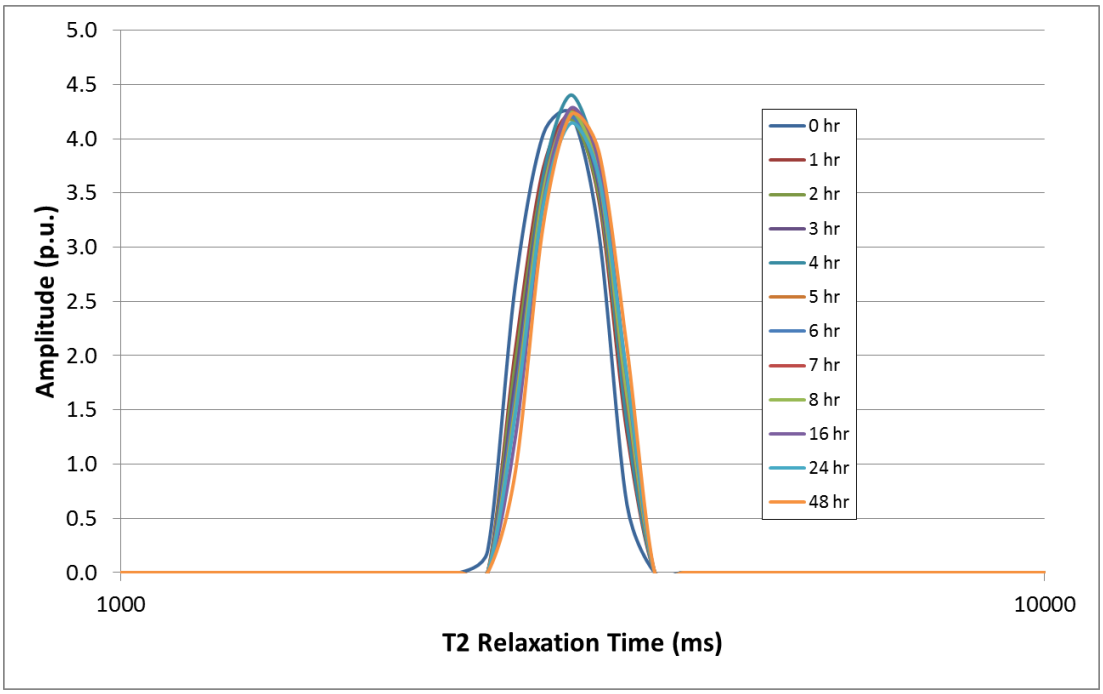

Figure 2: Collected T2 Spectra of liquid cyclopentane over 2 days to establish a baseline in NMR response for bulk cyclopentane fluid in our laboratory conditions.

Hydrate dissociation was then allowed to occur within a vacuum sealed vial of cyclopentane hydrate. A batch process of NMR experiments were collected at 15 minute intervals for an hour, followed by measurements performed at 1 hour intervals for the next 24 hours during dissociation of the hydrate species. Corresponding NMR spectra were then plotted to see respective changes in NMR response during this dissociation (Figure 3).

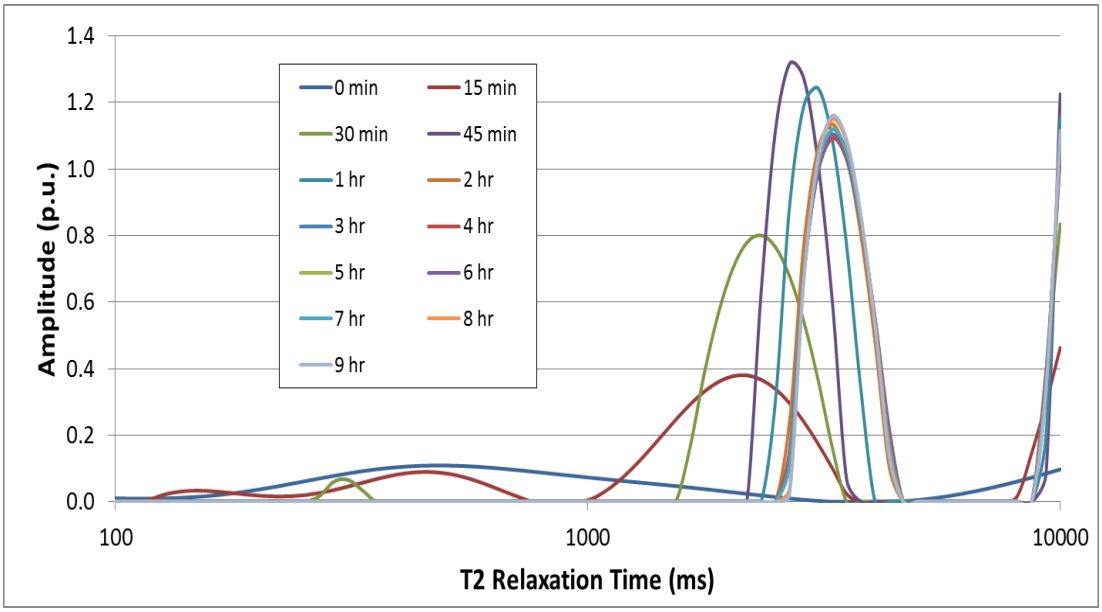

Figure 3: Collected T2 spectra of dissociating Cyclopentane hydrate in a vacuum sealed vial

Upon inversion of the raw T2 relaxation data, we observed that a relaxation peak in the time range greater than 8000 ms grew as the hydrate dissociated. This peak was not observed for the pure cyclopentane liquid sample T2 relaxation data at laboratory conditions which showed a relaxation peak at 3500ms as shown in Figure 2. The dissociated hydrate formed a meniscus between dissociated and undissociated hydrate in the sealed vial (Figure 4). We postulate that the partial pressure from cyclopentane hydrate dissociation might cause resonance at this fluid interface, contributing to the late time response of the NMR hydrate during dissociation.

Figure 4: Partially dissociated cyclopentane hydrate. This stable condition is marked by the presence of an interface between two different fluids that might cause the late time responses in recorded NMR T2 spectra.

NMR experiments were then performed at hour intervals for the following 48 hours to record any subsequent change of NMR T2 spectra and to observe if any further dissociation was occurring (Figure 5). We observed that no changes have occurred in the recorded spectra for the partially dissociated, yet stable cyclopentane hydrate.

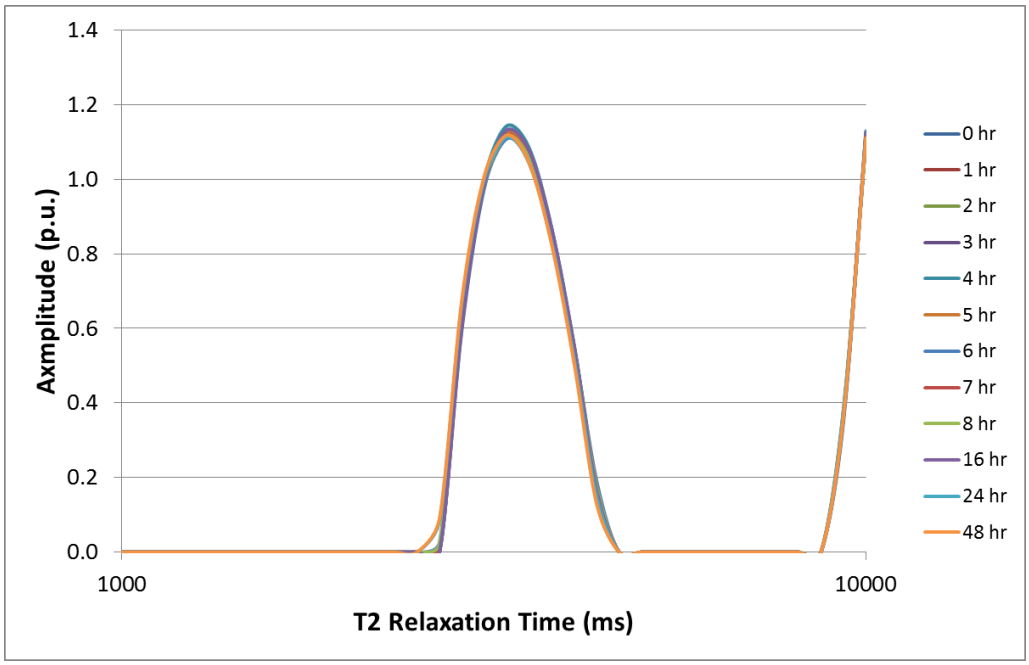

Figure 5: Stable NMR T2 spectra for stable partially dissociated cyclopentane hydrate. The late time peak is believed to be caused by resonance between fluid interfaces, but has not been verified.

Further exploration into this late time response in NMR T2 spectra is being investigated.

2.3. Improvements in Micro X-ray CT Imaging under Confining Pressure

We are implementing a pressure and temperature control system for use inside the Xradia-400 µCT machine. The goal of this work is to make µCT images of hydrate-bearing sediments while pore and confining pressure is applied. The temperature control is mainly intended for scans of gas-hydrate bearing sediments. In addition to pressure and temperature control we plan to conduct ultrasonic P-wave velocities simultaneously with µCT imaging. The combination of imaging and velocity measurements will give us insight in pore-scale changes in the rock and their influence on elastic properties.

We improved the confining pressure stability and are now able to hold a confining pressure of 13.8 MPa (2000 psi) for periods of more than 20 hours leading to a significant improvement in µCT image resolution to 5 µm.

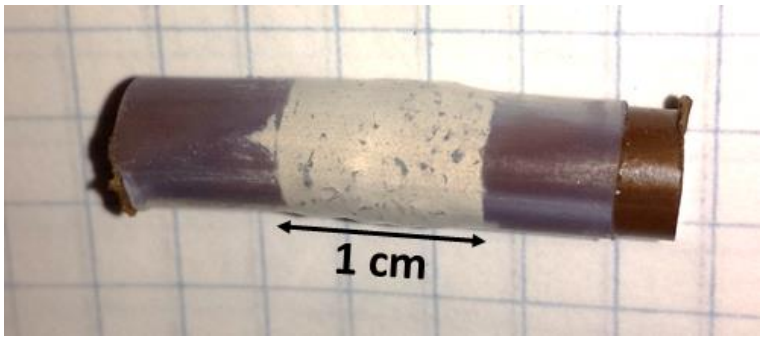

Figure 6: Sample of coarse-grained quartz sand with 30wt% bentonite between Torlon end pieces and heat-shrink jacket and artefacts in the CT images.

The sample shown in Figure 6 consists of a 1-cm long sediment pack placed between two Torlon end pieces which will later be replaced by the ultrasonic transducers. The sample was jacketed with heat-shrink tubing and clamped with steel wires on both ends. As sediment we used coarse grained quartz sand mixed with 30wt% bentonite. The sample was dry; pore pressure was not applied for these initial tests.

We conducted 3 cycles of confining pressure increase to 13.8 MPa (2000 psi) and subsequent decrease to atmospheric pressure. The confining pressure was increased for 16 hours before imaging and decreased back to atmospheric pressure for 8 hours prior to imaging to allow the sample to equilibrate. Multiple pressure cycles were performed to observe if the changes to the sample are reversible and whether there are further changes in a pre-compacted sample when pressurized again.

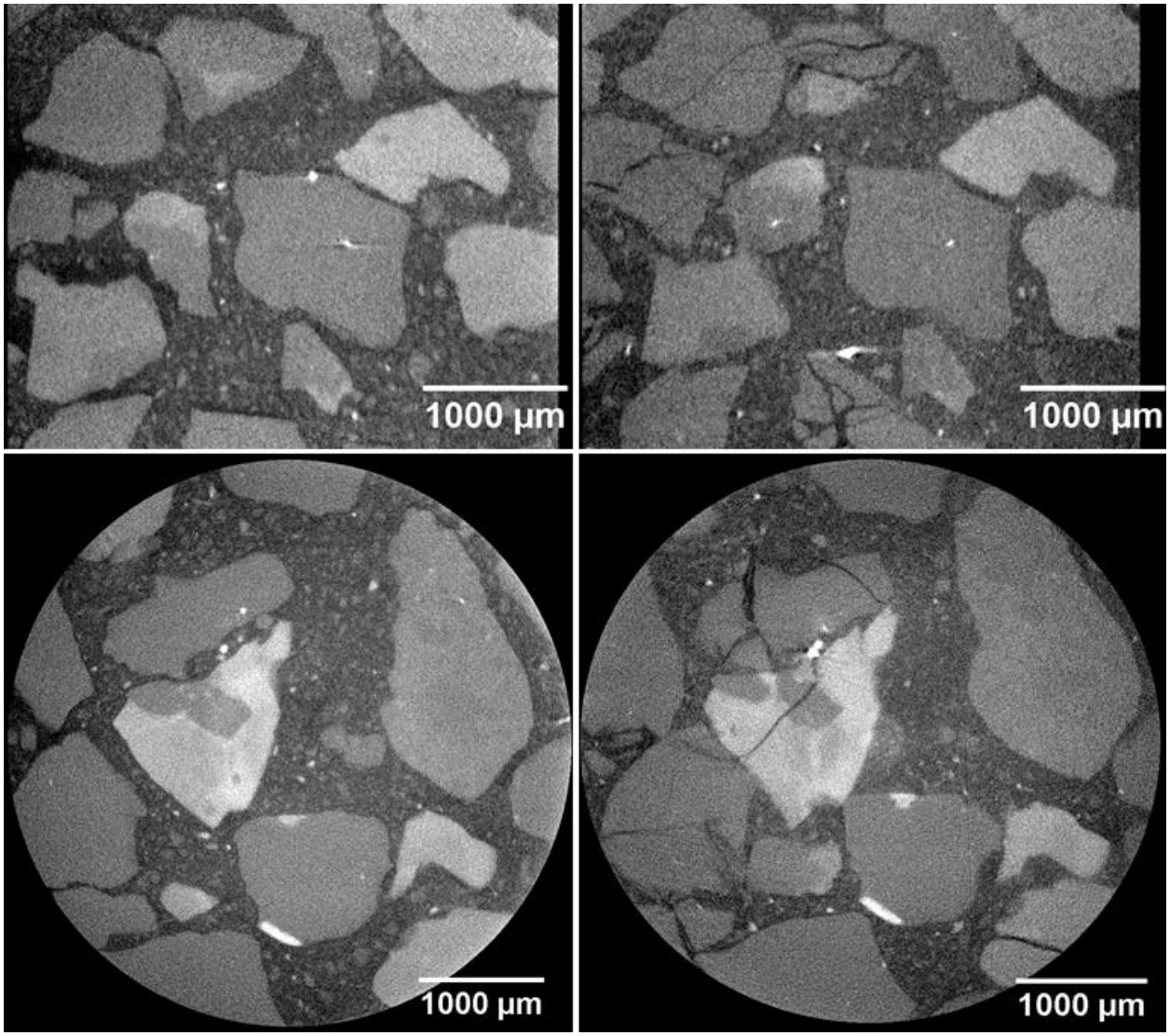

Figure 7: Vertical (top) and horizontal (bottom) slices of µCT images at atmospheric pressure (left) and 13.8 MPa (2000 psi) confining pressure (right). The images clearly show changes in the sample due to pressurization: grain crushing with associated fracturing was observed especially where quartz grains had direct contact points without clay-filled pore space in between.

Figure 7 shows vertical and horizontal slices through the sample. For comparison, we are showing images at atmospheric pressure prior to compaction and at 13.8 MPa confining pressure. We were able to observe grain damage throughout the entire sample, especially in quartz grains that had direct contact points. Grains that were separated by pore space at atmospheric pressure appear to be crushed against each other at elevated pressure which leads to fracturing.

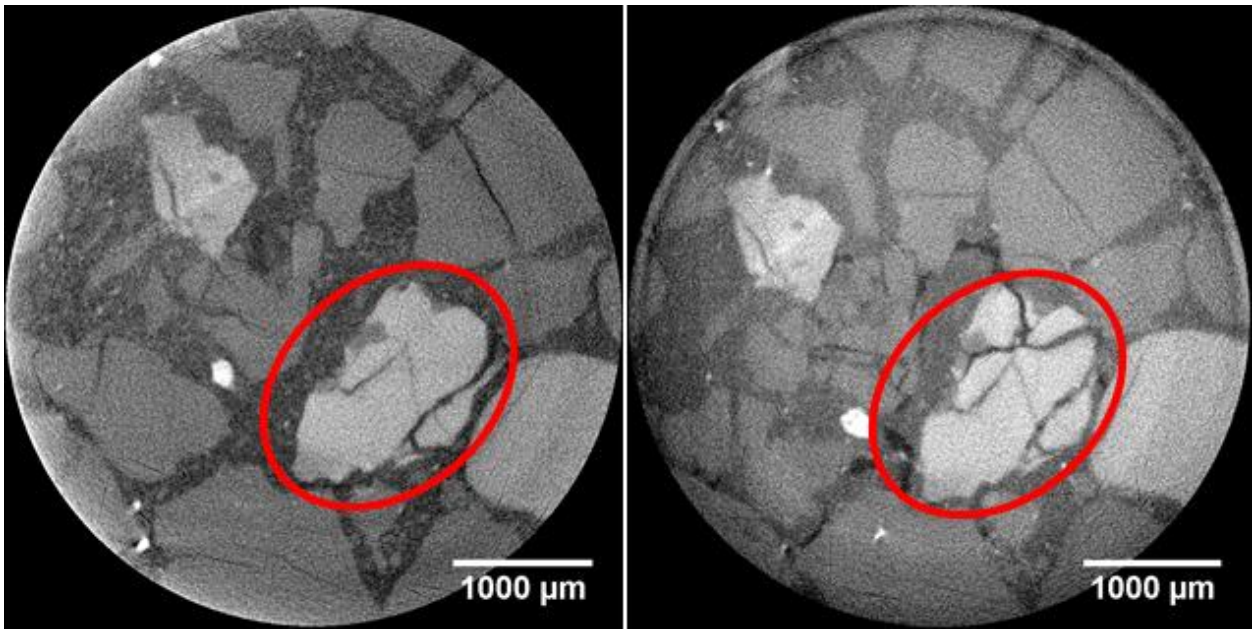

Figure 8: µCT images during first confining pressure increase to 13.8 MPa (2000 psi) (left) and after subsequent decrease to atmospheric pressure. We observed a further progression of existing fractures and opening of new fractures after the confining pressure was decreased between subsequent pressure cycles.

Figure 8 shows the comparison between an image taken during the first pressure cycle at 13.8 MPa and a subsequent image taken at atmospheric pressure. For some grains we observed that pre-existing fractures extended further and new fractures occurred upon decreasing the confining pressure. Some fractures also extended further upon repeated increase of confining pressure pointing to the conclusion that pre-compacted samples experience further change when subjected to increased confining pressure again.

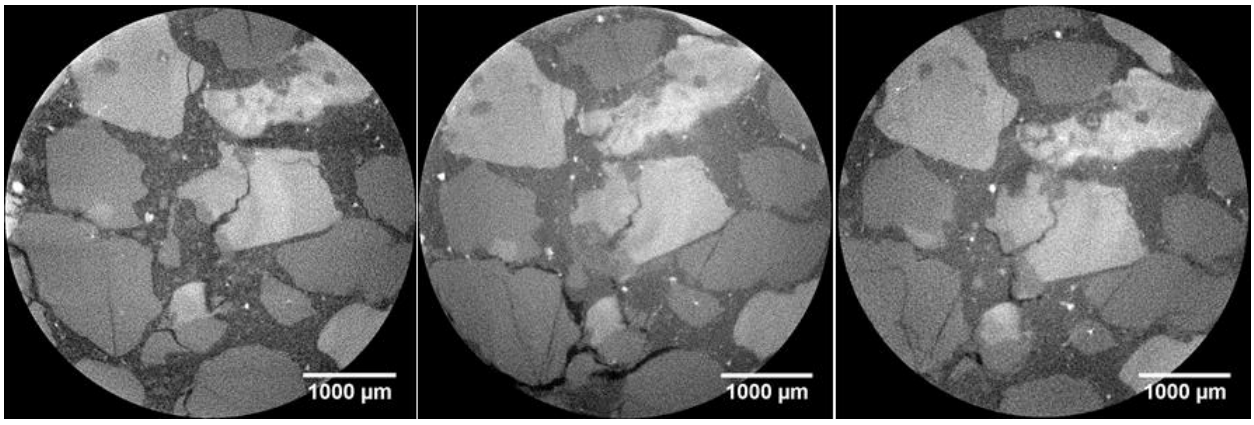

Figure 9: µCT images during first confining pressure increase to 13.8 MPa (2000 psi) (left), after subsequent decrease to atmospheric pressure (middle) and at atmospheric pressure after second confining pressure increase to 13.8 MPa (right). We observed the formation of void spaces especially at quartz grain surfaces (lower half of middle image). As the sample was confined, the clay in the pore

spaces was compressed resulting in a volume reduction. The sample expands again after decreasing the confining pressure while the clay stays compacted resulting in voids in the pore space.

Figure 9 shows images taken during the first pressure cycle at 13.8 MPa, after decreasing the pressure back to atmospheric pressure during the first cycle and after decreasing the pressure back to atmospheric pressure after the second pressure cycle. The bentonite clay in the pore space is compacted upon the application of confining pressure. When the confining pressure µCT imaging under confining is decreased, the clay stays compacted resulting in a decreased volume which leads to the formation of void spaces especially at the grain surfaces of quartz grains. This observed detachment of grains and pore filling materials could potentially lead to decreased stiffness of the sediment. Upon repeated confining pressure cycling these voids seemed to be partially closed again while new ones occurred in other areas of the sample.

2.4. Ultrasonic and Complex Resistivity Measurements

In this quarter we updated the equipment used to form hydrates out of the free gas stage, as reported in the previous report. We added feed-throughs with electric wires which will not just allow us to collect ultrasonic waveforms but also enable us to perform complex resistivity measurements. The updated pressure vessel with feed-throughs has been pressure tested and over a time of 24h. Furthermore, we started preparing nine cores. Three Foxhill sandstone samples, three Castlegate sandstone samples, and three Bishop Tuff samples were cut into one inch diameter and two inch length cylinders with holes drilled to host electrodes.

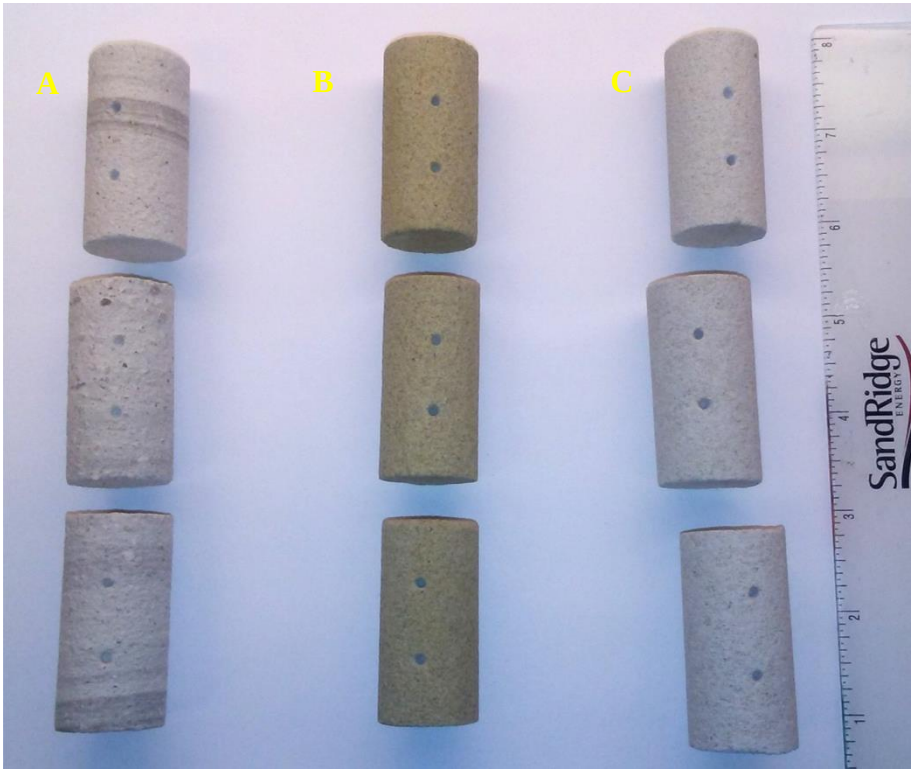

Figure 10: Sample overview for complex resistivity measurements. (A) Bishop Tuff, (B) Castlegate Sandstone, and (C) Foxhill Sandstone

We have covered the ends of the core samples with conducting epoxy and attached wires to the surfaces. After the samples are fully prepared and oven dried, we plan to put the samples into a desiccators with 100% humidity. This will cause a thin layer of water to cover the grain surfaces. Over time the sample should become fully saturated with water vapor which we will determine by periodically measuring the weight of the samples. Once the weight is stabilized, the samples will be put into the updated pressure vessel, pressurized with methane, and cooled below the methane hydrate stability temperature. Complex resistivity measurements. In theory, the hydrates will start forming at the gas – water interface and over time the hydrates will grow towards the grain surfaces. The formation of hydrates will cause a change in resistivity and a drastic velocity increase according to the envelope cementing model.

3. Acknowledgments

This project is funded by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) under Grant Number DEFE0009963. This project is managed and administered by the Colorado School of Mines and funded by DOE/NETL and cost-sharing partners.

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, NMR measurements and MXCT scanning. We are delayed in Milestone 7. However, due to various delays in our experimentation and initial attempts failing to form methane out of the free gas phase, we anticipate a more realistic completion date of 12/31/2016.

We are currently working on feed-throughs for fluid lines and electric wiring to use ultrasonic transducers and pressure control in combination for our MXCT experiments. Further we plan to include pore pressure in addition to confining pressure into the system. The pressure control system in combination with ultrasonic transducers will allow to visually observe pore scale changes in rock samples (such as crack closure, grain damage, porosity reduction, changes in saturation) while simultaneously identifying their influence on ultrasonic velocities. Such pore-scale changes are usually not taken into account by rock physics models and could help to identify why laboratory data diverges from theoretical models. Further, it is possible to compute compressibility from µCT images at different stress states by image correlation (Lenoir et al., 2007; Dautriat et al., 2011; Fusseis et al., 2014).

Pressure and temperature controls are currently being developed for future hydrate studies in the NMR machine.

The samples for the complex resistivity measurements will be oven dried and saturated with 100% humidity before they will be measured. After successfully forming methane hydrates we plan on injecting CO2 to perform a CH4 – CO2 exchange and monitor the mechanical and electrical changes.

Table 2: Q14 Milestones and Deliverables

Milestone	Task	Description	Completion date	Report Content
7	6	Methane hydrates from free gas phase (delayed)	12/31/2016	Progress report
10	9	NMR/MXCT characterization	9/30/2016	Progress report
13	12	Information Dissemination	12/31/2016	Progress report

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Dautriat, J., M. Bornert, N. Gland, A. Dimanov, and J. Raphanel, 2011, Tectonophysics Localized deformation induced by heterogeneities in porous carbonate analysed by multi-scale digital image correlation: Tectonophysics, 503, 100–116.

Fusseis, F., X. Xiao, C. Schrank, and F. D. Carlo, 2014, Review article A brief guide to synchrotron radiation-based microtomography in (structural) geology and rock mechanics: Journal of Structural Geology, 65, 1–16.

Lenoir, N., M. Bornert, J. Desrues, P. Besuelle, and G. Viggiani, 2007, Volumetric Digital Image Correlation Applied to X-ray Microtomography Images from Triaxial Compression Tests on Argillaceous Rock: 193–205

5. Products

Publications (Publications; Conference Papers, Presentations, Books)
Pohl, M., Prasad, M., Batzle†, M. L., Ultrasonic Attenuation of Pure THF-Hydrate: *Geophys. Prosp*. (revised and resubmitted).
Schindler, M., Batzle†, M. L., Prasad, M., Micro X-Ray Computed Tomography Imaging and Ultrasonic Velocity Measurements in Hydrate-Bearing Sediments: *Geophys. Prosp.* (revised and resubmitted).

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:	**Carolyn Koh**
Project Role:	Co-Investigator
Nearest person month worked this period:	0.25
Contribution to Project:	Dr. Koh helped with CH4 hydrate experimental setup and 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:	**Weiping Wang**
Project Role:	Laboratory Manager
Nearest person month worked	1

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

Name:	**Mathias Pohl**
Project Role:	Ph.D. student
Nearest person month worked this period:	3
Contribution to Project:	Mr. Pohl prepared samples and pressure tested new 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)	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:	No
If traveled to foreign country(ies),	N/A
duration of stay:	N/A

Name:	**Ahmad Afif Abdul Majid**
Project Role:	Post Doctoral Scholar
Nearest person month worked:	1
Contribution to Project:	Dr. Majid helped setting up our experiment to form methane hydrates out of free gas
Additional Funding Support:	Center for Hydrate Research
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:	**Kurt Peter Livo**
Project Role:	Ph.D. student
Nearest person month worked:	0.5
Contribution to Project:	Mr Livo helped collecting NMR data.
Additional Funding Support:	OCLASSH & 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. T. Collett provided data and guidance on interpretation and application. He continues to publish numerous papers on hydrate properties.

7. Changes / Problems

We requested and were granted a no-cost extension until December 31, 2016. The extension was necessitated due to delays and disruptions in our scheduled work caused by a change in PI and the need to rebuild equipment. The older equipment was not suitable for methane hydrate work. We have built a new system and have completed pressure tests on the newly built system. Thus, we anticipate making our measurements on methane hydrates in the coming months.

8. Special Reporting Requirements

None

9. Budgetary Information

Attached separately