DOE Award No.: DE-FE-0009963

Quarterly Research Performance Progress Report (Period ending 06/30/2016)

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

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

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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 quarter, we prepared samples of Castlegate sandstone, Fox Hills sandstone and Bishop tuff for the formation of methane hydrate and complex resistivity and ultrasonic velocity measurements during the hydrate formation.

We successfully formed methane hydrate in a Bishop tuff sample and measured complex resistivity during the formation and dissociation process. The data show a decrease in both real and quadrature conductivity as the hydrate forms and a decrease as hydrate dissociates, respectively. A more thorough analysis of the experimental data in context with the theory will follow. We will look deeper into establishing a quantitative relationship between complex conductivity and hydrate saturation as we perform more complex conductivity measurements on more samples.

The measurement procedure, sample descriptions and preliminary results for complex resistivity measurements are presented in this report.

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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 Q15 (Q3 of Year 4), we continued our work on Task 9 – MXCT Characterization and Task 6 – CH4-hydrate bearing rock (free gas).

With our success in Task 6, we can now move forward to Tasks 7 and 8 to investigate effects of hydrate formation method as well as CH_4-CO_2 replacement on acoustic and electrical properties.

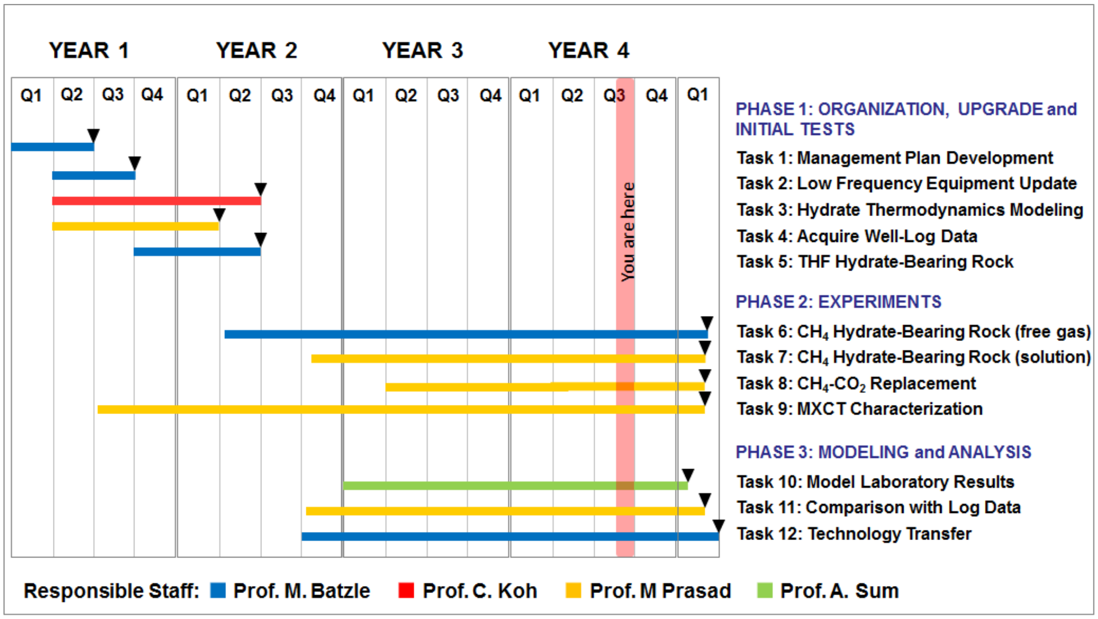

Figure 1: Milestone Status. We are at the end of our 15th quarter and in the final phase of this project. In February 2016, we requested and were granted a no-cost extension until December 31, 2016.

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	Planned	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 Complex Resistivity Measurements on Methane-Hydrate Bearing Samples

Experimental Description and Step-by-Step Procedure

The experiments comprise electrical measurements before, during, and after hydrate formation in three different rock samples. The purpose of this research is to experimentally observe the change in resistivity due to hydrate formation. In total, nine samples have been prepared – three Castlegate Sandstones, three Fox Hills Sandstones, and three Bishop Tuff samples. All samples were cut into cylinders with one inch diameter and two inches length. After the samples were prepared they were placed into a vacuum oven to completely dehydrate the samples.

The first experiments are conducted when the samples are dry. These first measurements are taken as a baseline and are compared with the measurements after hydrate formation to determine full conversion of water into methane hydrates.

After the samples are measured dry they are placed into a desiccator with 100% humidity. The samples absorb the moisture. This absorption is monitored by measuring the relative weight gain for each sample (Table 1).

All the measurements mentioned before are performed at room temperature and atmospheric pressure. To initiate hydrate formation, the samples are placed into a pressure vessel equipped with wire feed-throughs which allow us to perform the electrical measurements under pressure. After the sample is placed into the vessel and connected to the electrical wires it is pressurized with methane up to 1200 psi. Once the pressure is reached the samples will be measured again. The pressure vessel is submerged in a cooling bath for temperature control. To induce hydrate formation the temperature is decreased to 1 °C. Once the temperature and pressure conditions are suitable for hydrate formation, continuous measurements are conducted to record the change in resistivity due to hydrate formation.

Micro Structure of Complex Resistivity Samples

Castlegate Sandstone is a fluvial sandstone consisting mainly of quartz with a porosity of 21% (Figure 2) and permeability around 1 Darcy. Fox Hills Sandstone is a deltaic sandstone with significant clay content. Its porosity is around 28%, however, the permeability is lowered to around 50 mD due to the clay content (Figure 3).

Bishop tuff is a volcanic ash deposit with varying porosity. Near the top of the deposit porosities are as high as 37% towards the bottom (120 m burial depth) porosities decrease to 4%. The CT images reveal that this rock is more heterogeneous than the two sandstones (Figure 4). Grain size is highly variable with a lot of very fine grained material limiting pore connectivity and indicating low permeability. We will determine the exact porosities of the samples with specialized core methods used to measure porosity in shales and mudrocks (gas adsorption, NMR, water immersion).

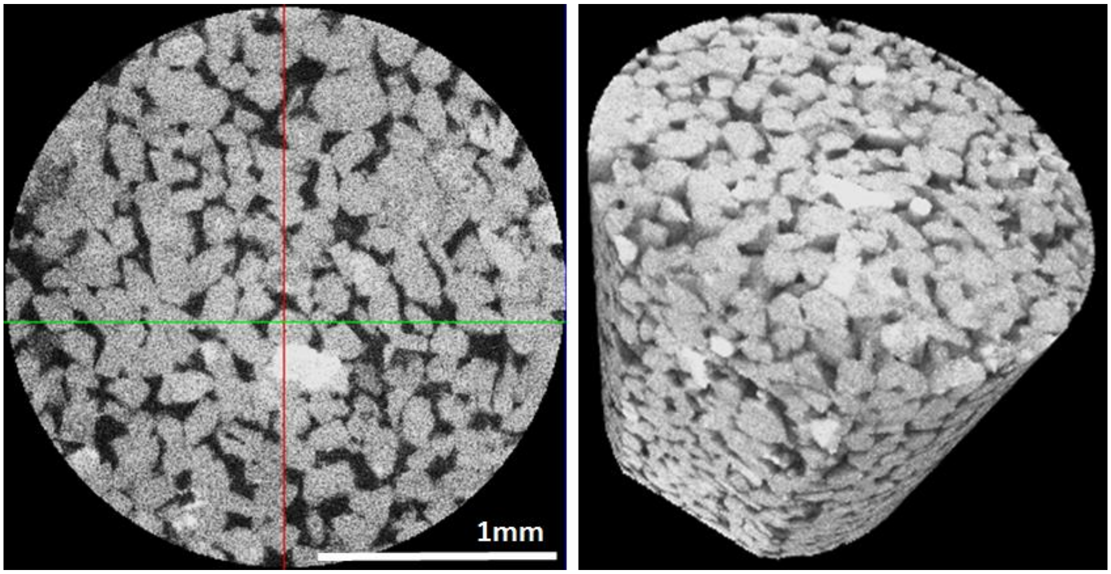

Figure 2 Micro CT image of Castlegate Sandstone- cross sectional view and 3D view

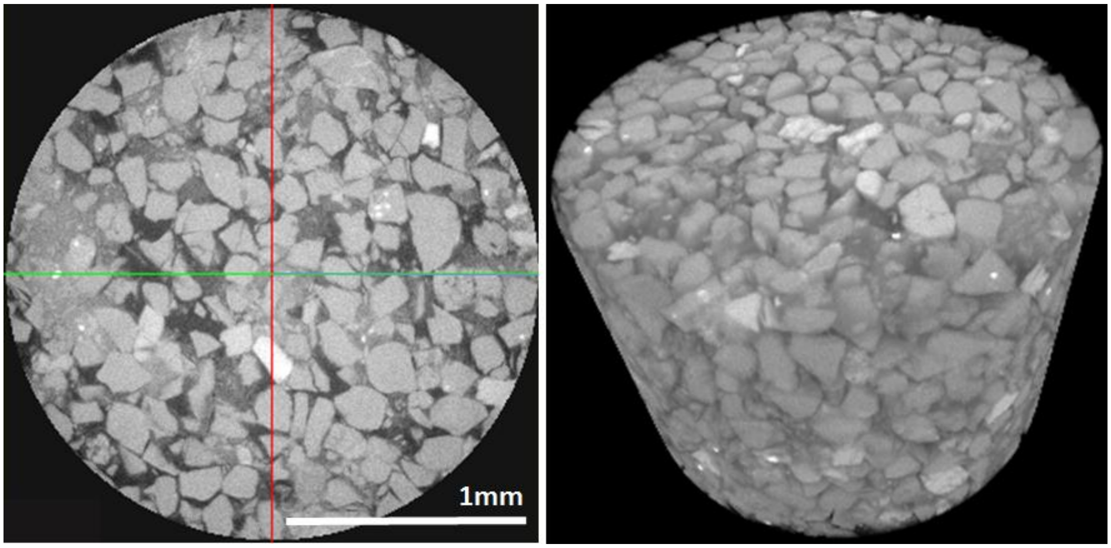

Figure 3 Micro CT images of Fox Hills Sandstone – cross sectional view and 3D view

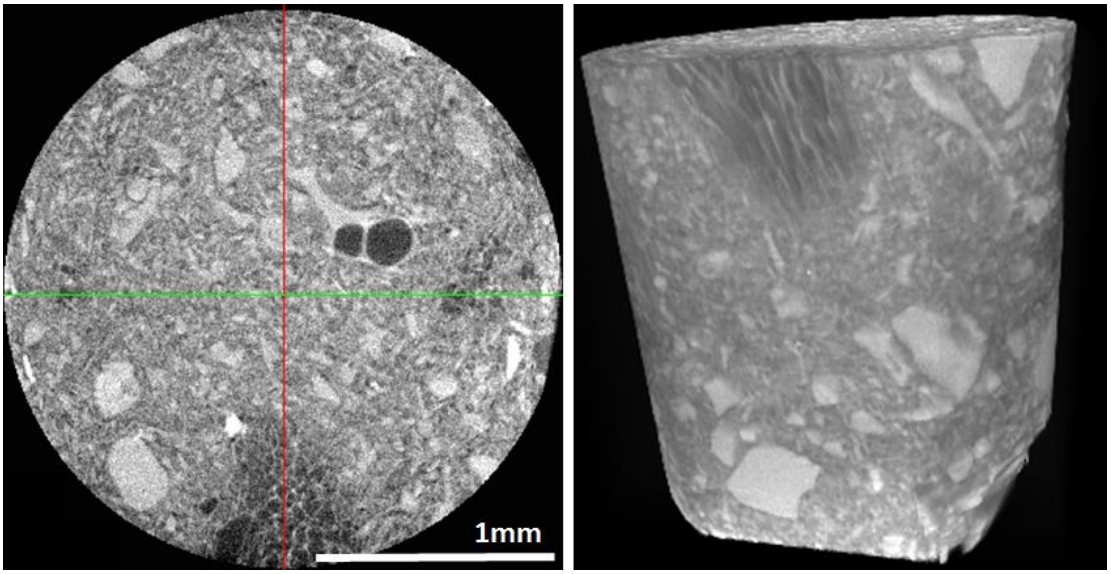

Figure 4 Micro CT images of Bishop Tuff – cross sectional view and 3D view

Estimated Water and Methane-Hydrate Saturations

The samples were humidified at 100% humidity for several days to weeks. For the calculations of water saturation and hydrate saturation shown in Table 2 we used a sample volume of 25.74 cc, the measured weight difference between wet and dry samples, a density of 0.9 g/cc for methane hydrate, 21% porosity for Castlegate sandstone and 28% porosity for Fox Hills sandstone. For the Bishop tuff samples the lower and upper limit of the porosity were used (4% and 37%). The hydrate saturation values are based on the assumption of full conversion of all present pore water.

Table 2: List of complex resistivity samples

sample	mass [g]		Vwater [cc]	Swater[%]		Shydrate [%]	
	dry	wet					
CG1	51.71	52.19	0.48	8.88		11.39	
CG2	53.48	54.48	1	18.50		23.74	
CG3	49.3	50.12	0.82	15.17		19.47	
FH1	56.21	57.31	1.1	15.26		19.59	
FH2	56.92	58.02	1.1	15.26		19.59	
FH3	49.25	50.19	0.94	13.04		16.74	
				for Φ=4%	for Φ=37%	for Φ=4%	for Φ=37%
VA1	40.25	40.42	0.17	16.51	1.79	21.19	2.29
VA2	40.66	40.86	0.2	19.43	2.10	24.93	2.69
VA3	39	39.15	0.15	14.57	1.58	18.69	2.02

Due to the large uncertainty in pore volume, water and hydrate saturation estimations for the Bishop tuff samples (VA1, VA2, VA3) vary by one order of magnitude. The amount of water absorbed by the tuff samples was small compared to the two sandstones which can be caused by low permeability or comparably lower porosity. Porosity measurements will restrain the saturation values.

Complex Resistivity Data for Sample VA2

We measured complex resistivity on 2 cores but had to aboard one of the experiments due to a leak in the pressure cell. Thus, we are presenting data for one sample of Bishop tuff (VA2).

Table 3: methane pump volume and calculated hydrate volume, the volume number represents the experimental stage

Volume #	Volume [cc]	Temp [C]	Volume of Hydrates [cc]
4	756.71	25	0
5	755.35	15	0
6	753.22	10	1.121
7	751.52	5	2.016
8	750.47	2.5	2.568
9	749.6	1	3.026
10	749.24	1	3.216
11	749.24	1	3.216
12	749.31	1	3.216
13	751.18	1	3.216
14	751.19	1	3.216
15	751.18	1	3.216
16	751.16	1	3.216

Figures 5, 6 and 7 show real conductivity, quadrature conductivity and real resistivity over the course of the entire experiment for one frequency. Complex resistivity was first measured at room temperature and atmospheric pressure outside of the pressure vessel. The sample was then placed in the pressure vessel and complex resistivity was measured again at room temperature and atmospheric pressure. It was then pressurized with methane gas to 1200 psi. To reach hydrate stability conditions the sample needed to be cooled below 14 C. The temperatures are measured outside of the pressure vessel in the cooling bath since our setup does not contain enough electrical wire feed-throughs to include a thermocouple in the pressure cell. We plan to add this critical measurement in the next quarter.

A drop in both real and quadrature conductivity was observed as the temperature was decreased below hydrate stability. The conductivities stabilized upon reaching 1 C and continued to decrease slowly over time as the sample was left at constant pressure and temperature conditions. This slow decrease in conductivity (from stage9 to stage 21) can be attributed to the ongoing conversion of water into methane hydrate. The variation of conductivities in these stages is possibly caused by temperature fluctuations.

During the temperature increase back to room temperature we observed an increase in conductivity which can be attributed to the dissociation of hydrate and the related increase of the amount of water in the pore space.

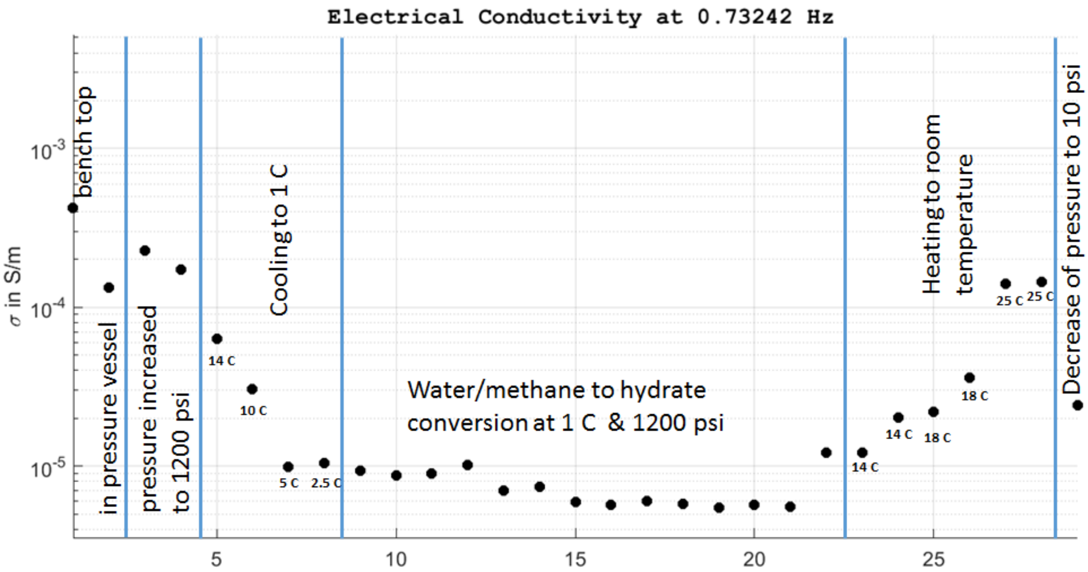

Figure 5: Real electrical conductivity for all 29 stages of the experiment including pressurization, cooling, hydrate formation, heating and depressurization at one frequency

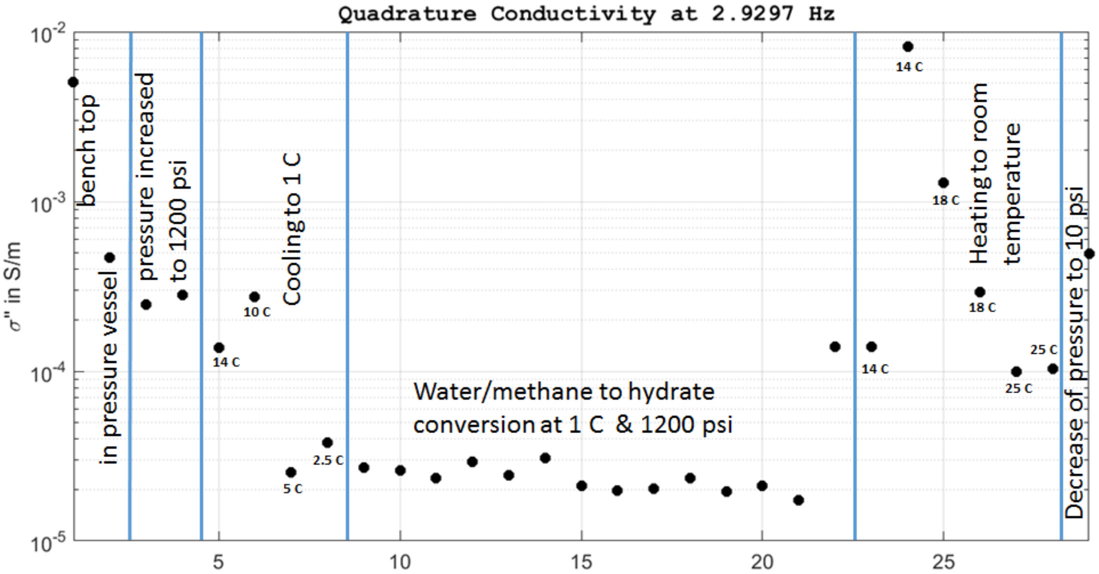

Figure 6: Imaginary (quadrature) electrical conductivity for all 29 stages of the experiment including pressurization, cooling, hydrate formation, heating and depressurization at one frequency

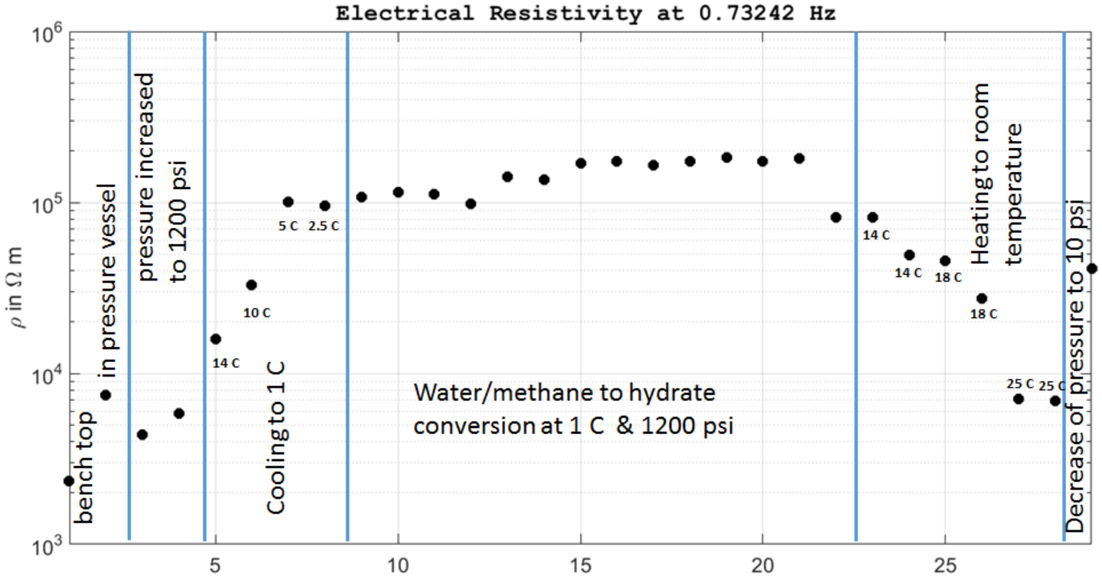

Figure 7: Real electrical resistivity for all 29 stages of the experiment including pressurization, cooling, hydrate formation, heating and depressurization at one frequency

Figures 8 and 9 show real and quadrature conductivity as a function of frequency. Real conductivity increases with increasing frequency while quadrature conductivity shows a local maximum at 0.1 Hz, then decreases and increases with increasing frequency for values higher than 10 Hz. This behavior is in agreement with data and models described by Revil et al. (2014). The paper describes how conductivity varies with frequency due to different physical processes dominating at different frequencies.

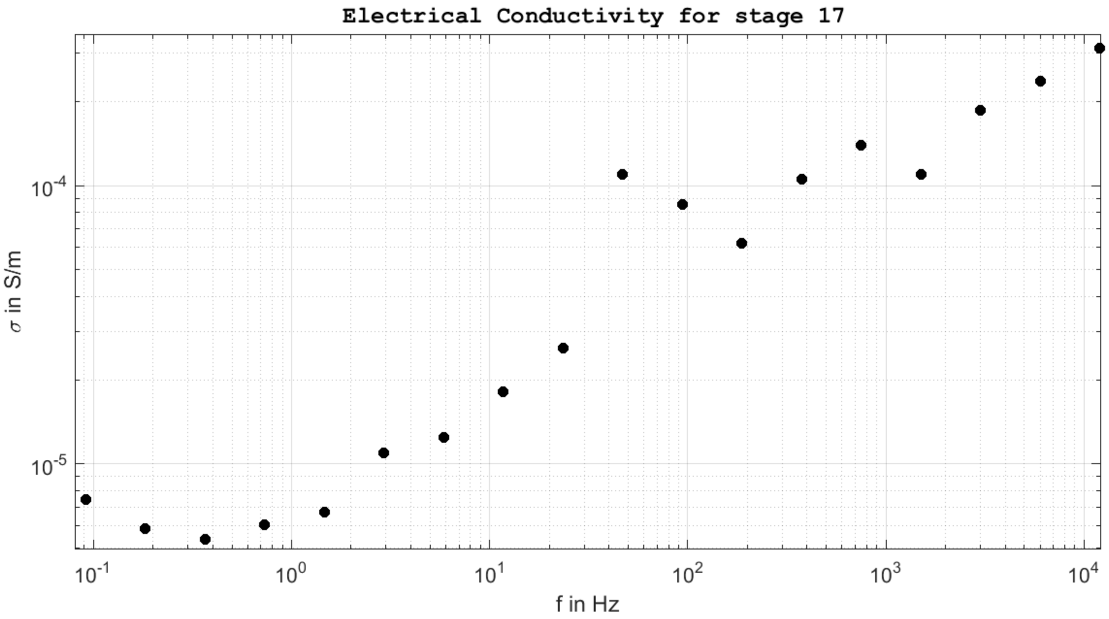

Figure 8: Real electrical conductivity for all 18 frequencies, shown for 1 experimental stage (1200 psi, 1 C)

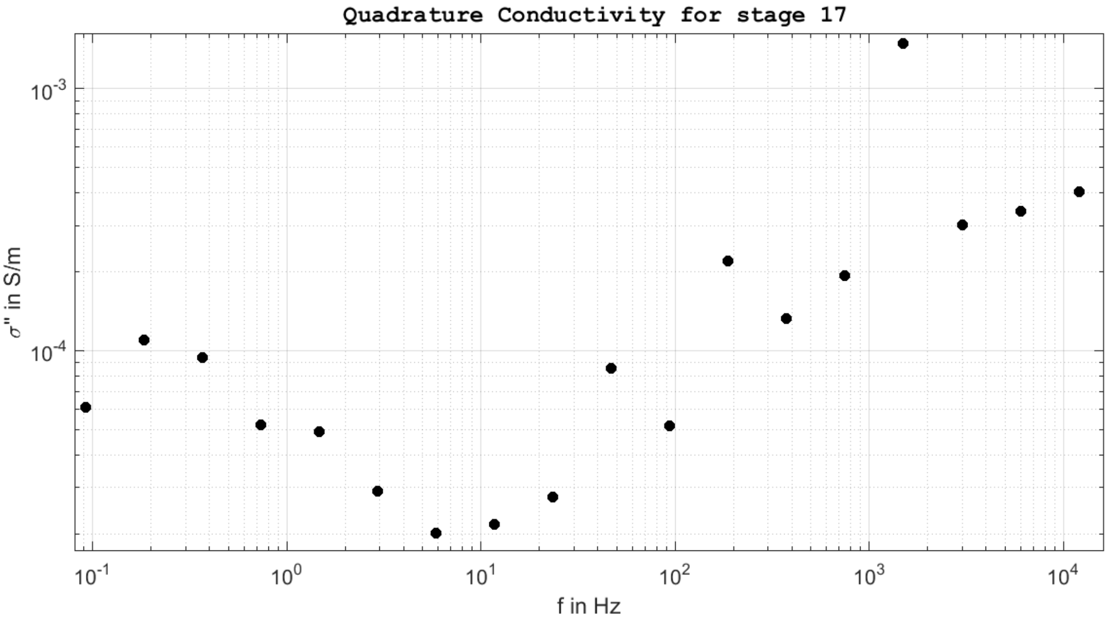

Figure 9: Imaginary (quadrature) electrical conductivity for all 18 frequencies, shown for 1 experimental stage (1200 psi, 1 C)

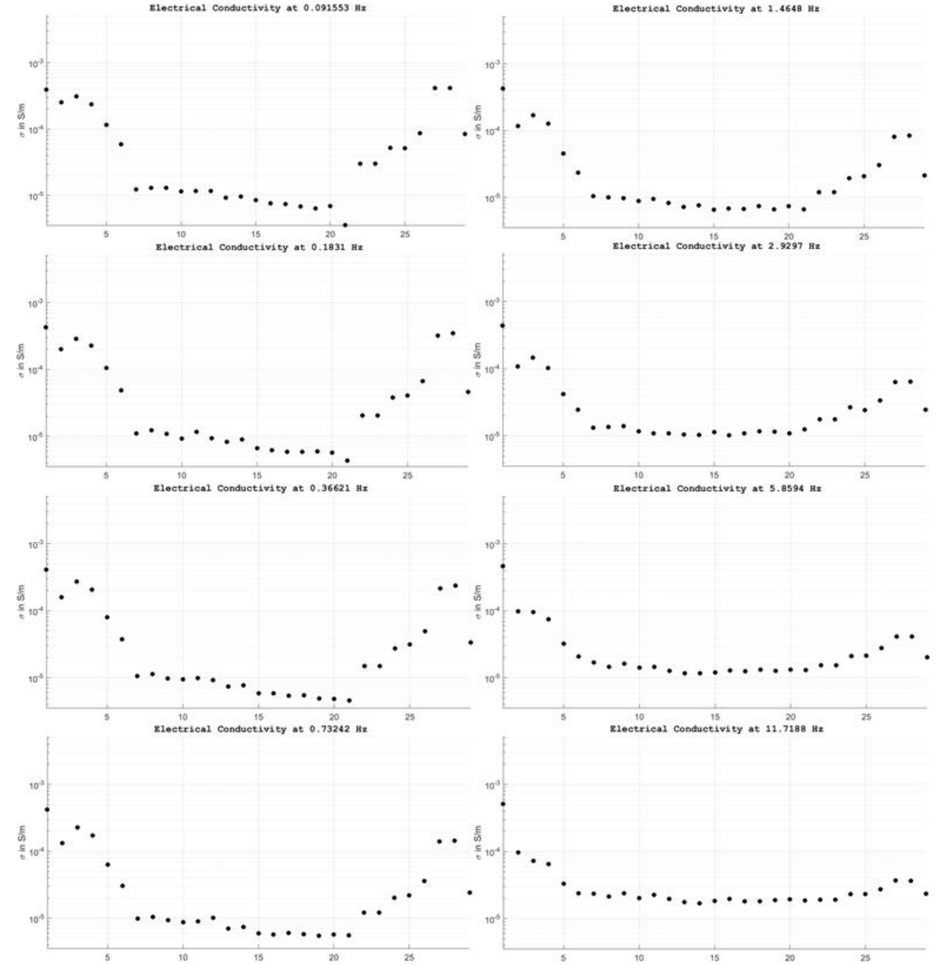

Figure 10: Real electrical conductivity for all 29 experimental stages, shown for 8 frequencies between 0.09 Hz (upper left) and 11.7 Hz (lower right)

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).

References

Revil, A, N. Florsch and C. Camerlynck (2014): “Spectral Induced Polarization Porosimetry”, *Geophysical Journal International*, GJI Marine geosciences and applied geophysics, Vol. 198, p. 1016-1033

4. Plans

Table 4 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. 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 formed methane hydrate in sediment samples and measured complex resistivity. We plan to repeat these measurements for more samples and further measure ultrasonic velocities on the same type of methane-hydrate bearing rock samples.

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 while simultaneously identifying their influence on ultrasonic velocities.

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

Table 4: 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

5. Products

Publications (Publications; Conference Papers, Presentations, Books)

Schindler, M. and Prasad, M.: “Micro X-ray CT imaging of sediments under confining pressure” – SEG expanded abstract, accepted for oral presentation at the SEG annual meeting in Dallas, October 18, 2016

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:	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:	**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 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:	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:	1
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:	Norway, Germany
If traveled to foreign country(ies),	N/A
duration of stay:	3 weeks

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

Name:	**Cesar Mapeli**
Project Role:	Ph.D. student
Nearest person month worked:	1
Contribution to Project:	Mr. Mapeli improved the CH4 hydrate setup and collect complex resistivity 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.

Mathias Pohl was interning for the months of May and June and thus had to interrupt his experimental work. Cesar Mapeli and Mandy Schindler continued his work on methane-hydrate bearing sediments.

8. Special Reporting Requirements

None

9. Budgetary Information

Attached separately