NATIONAL ENERGY TECHNOLOGY LABORATORY
OIL & GAS

DOE Award No.: DE-FE0009897

Quarterly Research Performance Progress Report
(Period Ending 06/30/2017)

Hydrate-Bearing Clayey Sediments: Morphology, Physical Properties, Production and Engineering/Geological Implications

Project Period (10/1/2012 to 9/30/2017)

Submitted by:
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U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Office of Fossil Energy

DISCLAIMER:

ACCOMPLISHMENTS

Context – Goals. *Fine grained sediments host more than 90% of the global gas hydrate accumulations. Yet, hydrate formation in clayey sediments is least understood and characterized. This research focuses on hydrate bearing clayey sediments. The goals of this research are (1) to gain a fundamental understanding of hydrate formation and ensuing morphology, (2) to develop laboratory techniques to emulate "natural" formations, (3) to assess and develop analytical tools to predict physical properties, (4) to evaluate engineering and geological implications, and (5) to advance gas production alternatives to recover methane from these sediments.*

Accomplished

The main accomplishments for this period include:

- THF hydrate in clayey sediments
    - Super-cooling temperature and morphology
    - Elastic properties
- Impacts of fines on hydrate formation and dissociation

Plan - Next reporting period

- Damping characteristics of hydrate in clayey sediments

RESEARCH IN PROGRESS

THF hydrate in clayey sediments

Supercooling temperature and hydrate morphology. THF is used as a proxy of hydrate formed in clayey sediments (i.e., kaolinite). Specimens are prepared by mixing kaolinite clay with certain amounts of 100% stoichiometric THF solution, i.e., mass ratio of H_2O:THF = 81:19. The solution and clay mass ratios are 50:100, 60:100, and 70:100 in this report. Since hydrate nucleation is a random process, THF hydrate formation occurs at different temperatures. In general, hydrates formed at lower supercooling temperatures tend to have lower hydrate saturation and be closer to core boundaries; while hydrates formed at higher supercooling temperatures manifest across the whole specimen and more hydrate volume even initial mass ratios are identical (Figure 1).

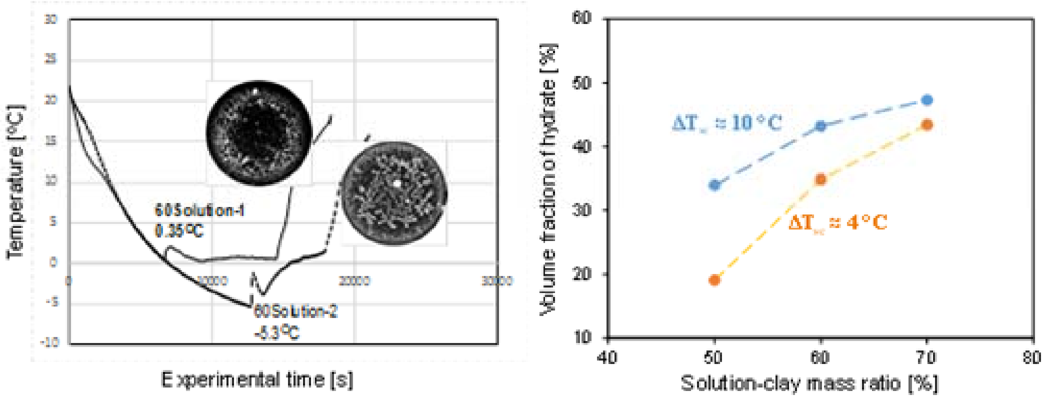


Figure 1: (Left) Temperature signatures and X-ray images of two specimens with identical initial mass ratio of 100% stoichiametric solution and clay (i.e., 60:100 in this case). Hydrates formed at lower temperature, i.e., higher supercooling, tend to render higher volume than that formed at lower supercooling. (Right) Volume fraction of hydrate to clay formed using three different initial mass ratios and supercooling temperature. Higher hydrate saturations are observed in specimens experienced higher supercooling. Note that as THF hydrates formed in clayey sediments are segregated, hydrate saturation is more appropriatedly defined as the total volume of hydrate over the total volume of the specimen.

Elastic properties. Both p- and s-wave signatures are collected during hydrate formation and dissocaition processes for all tested specimens. These data allow determining all elastic (i.e., Young's, shear, bulk, and constrained) moduli in clayey sediments with various hydrate saturations. Absolution wave velocities and elastic moduli values will be reported in next report, together with damping characteristics.

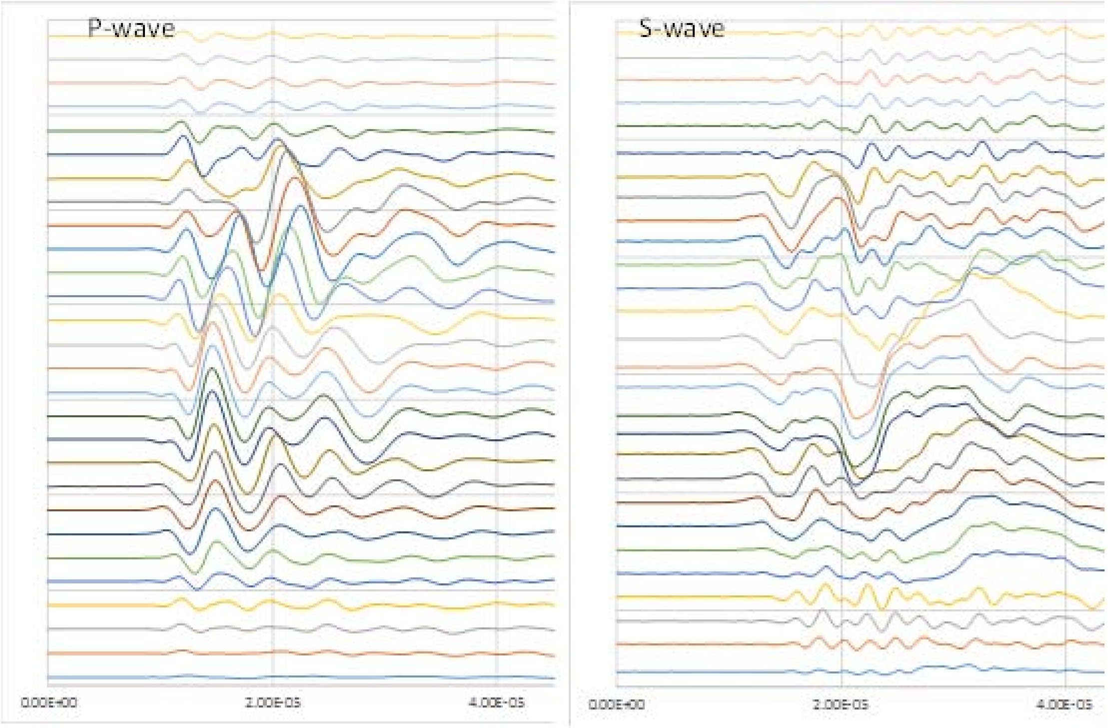


Figure 2: Cascades of p- and s-wave signatures collected throughout the experiments. Results allow computing not only wave velocities but also all elastic properties of clayey sediments with various hydrate saturations.

Impacts of fines on hydrate formation and dissociation

The impacts of fines content on hydrate formation are studied by using sandy specimens with 0, 5, 10, and 15% by mass of kaolinite. Hydrate formation is triggered via cooling followed by pressurization, which may cause preferential hydrate formation at core boundaries. This is done purposely to learn whether the presence of fine particles can suppress the preferred hydrate formation caused by cooling-pressurization process. Results show that the presence of fine-grained particles does not efficiently suppress water migration during hydrate formation. However, the presence of fines does affect the uniformity of packing with a general trend of being less uniform for specimens with higher fines content (Figure 3). Sands tend to agglomerate in patches by fine-grained particles mixed with water; and thus, after hydrate formation, the specimen with 15% fines appears patchier than that with no fine-grained particles. Admittedly, the initial packing (dense versus loose), which is also affected by fines content, should have an impact on the final packing after hydrate formation.

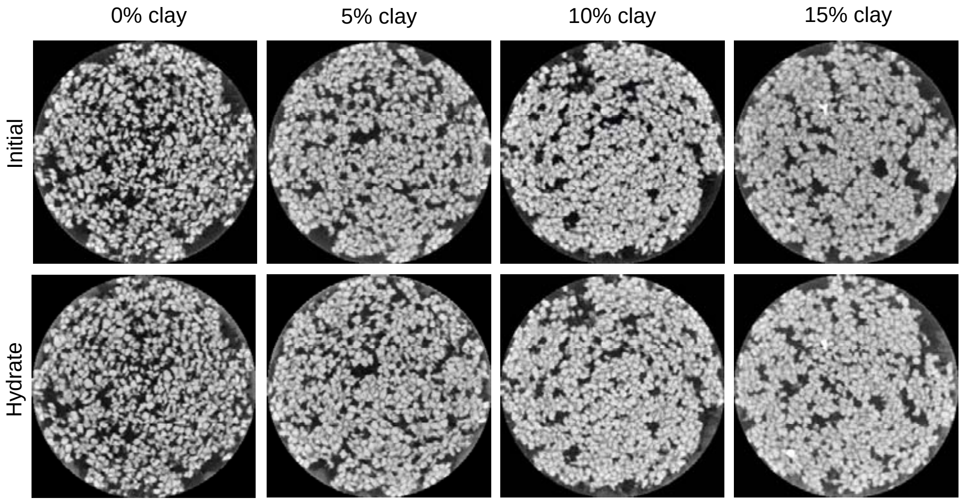


Figure 3: X-ray CT images of sandy specimens with different fines content by weight before and after hydrate formation. The presence of fines tend to 'agglomerate' sandy partilces and form larger patches.

Fine-grained particles tend to adsorb water on its surface and decrease water activity; thus, less free water will be converted to form hydrate. This is also true in THF hydrate formation in kaolinite as shown in previous section of this report. Experimental results show that for specimens with identical water content, those with higher fines content render less gas consumption for hydrate formation or lower water to hydrate conversion ratio.

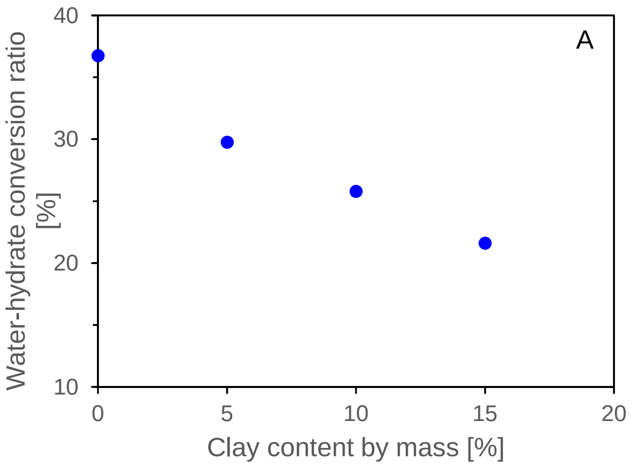


Figure 4: Water to hydrate conversion ratio decreases with increasing fines content in the specimens, as clayey particles absorbe water mocules on their surfaces and decrease water activity.

MILESTONE LOG

Milestone	Planed completion date	Actual completion date	Verification method	Comments
Literature review	5/2013	5/2013	Report	
Preliminary laboratory protocol	8/2013	8/2013	Report (with preliminary validation data)	
Cells for Micro-CT	8/2013	8/2013	Report (with first images)	
Compilation of CT images: segregated hydrate in clayey sediments	8/2014	8/2014	Report (with images)	Additional studies in progress
Preliminary experimental studies on gas production	12/2014	12/2014	Report (with images)	
Analytical/numerical study of 2-media physical properties	5/2015	5/2015	Report (with analytical and numerical data)	
Experimental studies on gas production	12/2015	12/2015	Report (with data)	Additional studies in progress
Early numerical results related to gas production	5/2016	2/2016	Report	
Comprehensive results (includes Implications)	9/2016	9/2016	Comprehensive Report	

PRODUCTS

- **Publications & Presentations:**

Liu, Z., Kim, J., and Dai, S. THF hydrate in clayey sediments: formation, morphology, and elastic properties. (In preparation).

Jang, J., Sun, Z. and Santamarina, J.C., (2017). Capillary pressure across a pore throat in the presence of surfactants. *Water Resources Research*. (Published online).

Dai, S., and Santamarina, J.C., (2017). Stiffness evolution in frozen sands subjected to stress changes. *Journal of Geotechnical and Geoenvironmental Engineering* (Published online).

Park, J., & Santamarina, J. C. (2017). Revised Soil Classification System for Coarse-Fine Mixtures. Journal of Geotechnical and Geoenvironmental Engineering, (Published online).

Lei, L., Liu, Z., Seol, Y., Boswell, R. and Dai, S. (2017) Hydrate formation in an unsaturated system - Impacts of fine particles and water content. 9th International Conference on Gas Hydrate, Denver, CO.

Jang, J. and Santamarina, J.C., (2016). Hydrate bearing clayey sediments: Formation and gas production concepts. *Marine and Petroleum Geology*, 77, pp.235-246.

Shin, H. and Santamarina, J.C., (2016). Sediment–well interaction during depressurization. *Acta Geotechnica*, pp.1-13.

Dai, S., Shin, H. and Santamarina, J.C., (2016). Formation and development of salt crusts on soil surfaces. *Acta Geotechnica*, 11(5), pp.1103-1109.

Jang, J., & Carlos Santamarina, J. (2015). Fines Classification Based on Sensitivity to Pore-Fluid Chemistry. *Journal of Geotechnical and Geoenvironmental Engineering*, 142(4), 06015018.

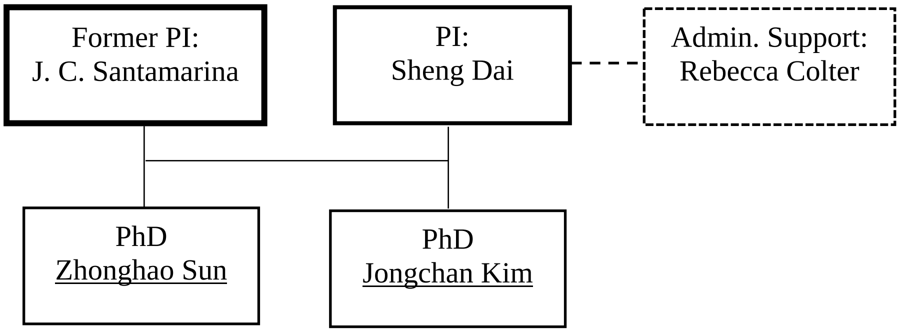
- **Website:** Publications and key presentations are included in http://pmrl.ce.gatech.edu/ (for academic purposes only)
- **Technologies or techniques:** X-ray tomographer and X-ray transparent pressure vessel
- **Inventions, patent applications, and/or licenses:** None at this point.
- **Other products:**

Lei, L (2017). Gas Hydrate in Fine-grained Sediments - Laboratory Studies and Coupled Processes Analyses. PhD Thesis, Georgia Institute of Technology.

PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS

Research Team: The current team involves:

- Carlos Santamarina (Professor)
- Sheng Dai (Assistant Professor)
- Zhonghao Sun (PhD student)
- Jongchan Kim (PhD student)



IMPACT

Understanding of fine grained hydrate-bearing sediments.

CHANGES/PROBLEMS:

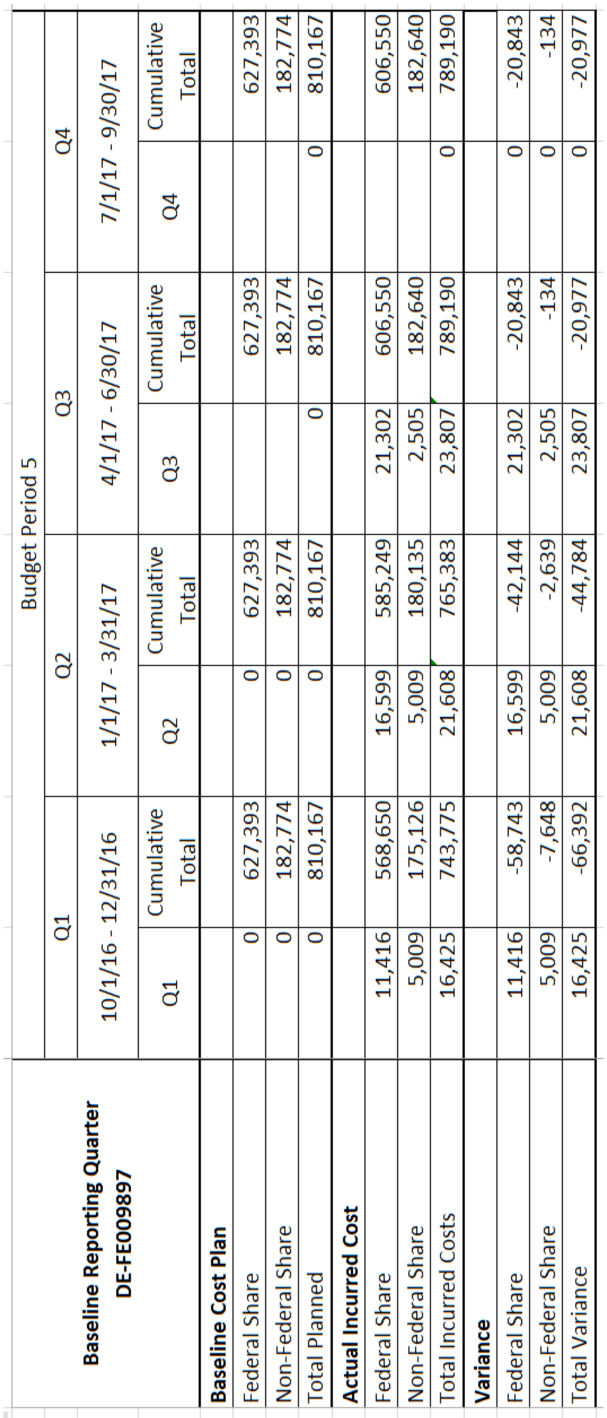
None at this point.

SPECIAL REPORTING REQUIREMENTS:

We are progressing towards all goals for this project.

BUDGETARY INFORMATION:

As of the end of this research period, expenditures are summarized in the following table. Note that the summer time for PI has not yet been reflected on this budget. The remainder of the fund will be zeroed by GRA support until September, 2017.



Baseline Reporting Quarter DE-FE009897	Budget Period 5							
	Q1		Q2		Q3		Q4	
	10/1/16 - 12/31/16		1/1/17 - 3/31/17		4/1/17 - 6/30/17		7/1/17 - 9/30/17	
	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total
Baseline Cost Plan								
Federal Share	0	627,393	0	627,393		627,393		627,393
Non-Federal Share	0	182,774	0	182,774		182,774		182,774
Total Planned	0	810,167	0	810,167	0	810,167	0	810,167
Actual Incurred Cost								
Federal Share	11,416	568,650	16,599	585,249	21,302	606,550		606,550
Non-Federal Share	5,009	175,126	5,009	180,135	2,505	182,640		182,640
Total Incurred Costs	16,425	743,775	21,608	765,383	23,807	789,190	0	789,190
Variance								
Federal Share	11,416	-58,743	16,599	-42,144	21,302	-20,843	0	-20,843
Non-Federal Share	5,009	-7,648	5,009	-2,639	2,505	-134	0	-134
Total Variance	16,425	-66,392	21,608	-44,784	23,807	-20,977	0	-20,977

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