# **Oil & Natural Gas Technology**

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**Quarterly Research Performance Progress Report (Period ending 09/30/2014)** 

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

Project Period (10/1/2012 to 9/30/2016)

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**Office of Fossil Energy** 

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#### 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 <u>hydrate bearing clayey sediments</u>. 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:

- Formation of CO<sub>2</sub> hydrate in fine-grained sediment with segregated topology, analogous to natural sediments using two separate methods
  - Injection of liquid CO<sub>2</sub>
  - Ice-to-hydrate transformation
- Numerical solution for large-strain stiffness with varying lens angles
- Implementation of a simplistic method of beam hardening correction for additional image processing

#### **Plan - Next reporting period**

Further develop and scrutinize hypotheses regarding the mechanism of hydrate formation in natural hydrate-bearing fine-grained sediments by distilling the information gained from the hydrate formation experiments conducted for the last 18 months. Advance numerical studies of the physical properties of hydrate-bearing fine-grained sediments. Test initial strategies for gas production from hydrate-bearing clayey sediment. Develop image processing techniques for optimum image presentation.

#### **Research in Progress**

#### CO<sub>2</sub> hydrate formation experiments

Additional hydrate formation experiments were performed using  $CO_2$  gas as the guest molecule, and were executed following two unique strategies: (1) liquid  $CO_2$  injection in saturated diatoms and (2) transformation of ice to hydrate.

# Liquid CO<sub>2</sub> injection

A similar procedure as documented in the previous report was followed by injecting liquid  $CO_2$  into a saturated diatom specimen loaded with a spring to apply effective stress. However, in this test, the rate and volume of injection was reduced to form finer fractures by which hydrate could gradually form and propagate in.





Figure 1. Fracture and hydrate growth evolution with time. The red numbers represent the day on which the image was captured. Notice fracture formation from 1-3, hydrate formation from 2-5, and hydrate dissociation from 6-8. Color code: yellowish-green = aluminum; lighter blue = diatoms; darker blue = hydrate/water; black = air



Figure 2. P-T path of the specimen. Notice in the exploded view the thermal spike signifying the exothermic hydrate formation reaction.

#### Ice-to-hydrate experiments

Another series of hydrate formation experiments were conducted with a different approach. The concept behind this set of experiments was to simulate visually a more analogous specimen (compare with experiments reported previously) to naturally occurring hydrate veins and lenses in fine-grained sediments identified by X-ray images of recovered pressure cores. For the first two trials, the idea was to mix kaolinite clay with water and then freeze it to form an initial ice lens structure; the ice would then be melted slowly by careful thermal control, and the ice would transform into hydrate assuming a supply of  $CO_2$  gas was present. For the final trial, a preformed ice lens was embedded into dry kaolinite, the chamber was pressurized with CO2, and the temperature was gently increased to allow for ice-to-hydrate transformation.

The experimental setup was altered to allow for better control for this specific set of tests, and the schematic is shown in the following figure 3.



Figure 3.  $CO_2$  hydrate formation experiment schematic. PT and TC represent the pressure transducer and thermal couples, respectively. The chamber on the right inside the environmental chamber acted as a temporary storage of gas to allow for gas temperature stabilization before injection and for better control over the injection rate.

**1. No applied stress on top of sediment** After freezing



Color code: bright green = aluminum; light bluish-green = clay; dark blue = ice

After hydrate formation

Color code: bright green = aluminum; bluish-green = clay; lighter blue = hydrate; dark blue/black = air



2. Stress applied on surface of sediment with spring



Color code: green = aluminum; lighter blue = clay; darker blue = ice; black = air



Color code: yellow = aluminum; green = clay; lighter blue = hydrate; dark blue = air; black = air



P-T response with relevant phase equilibria.

3. Initially prepared ice lens embedded in dry clay



 $1^{st}$  image: slice through center of preformed ice lens. Color code: yellow = aluminum; lighter blue = clay; darker blue = ice; black = air



Top Images: slice through center of bulk hydrate lens and through hydrate veins above lens; Color code: yellow = aluminum; bright green = dense clay; bluish-green = clay; blue = hydrate; black = air



PT response of the specimen

#### Numerically computed properties: Large-strain stiffness

Models of hydrate-bearing fine-grained sediments were created to numerically evaluate the evolution in elastic large-strain stiffness with varying hydrate lens angle, and the models were formed as analogs to natural hydrate reservoirs identified by X-ray images of pressure core samples. In total 5 cylindrical models were constructed with hydrate lens structures ranging from 0° to 90° in relation to the bottom plane. The size ( $\emptyset$ =100mm, H=200mm), lens thickness (a=4mm), and fraction of hydrate (18%) were kept constant for all models.



Lee et al. 2013 – Ulleung Basin

The simulations were completed in Abaqus. After verifying the models for one material with the elastic solution, as shown below, both hydrate and clay were modeled together and the stiffness of the hydrate-bearing sediment was shown to increase with increasing lens angle.



Input Parameters									
Property	Material								
	CH <sub>4</sub> Hydrate	Clay (Kaolinite)							
Density, $\rho$ [kg/m <sup>3</sup> ]	930 <sup>b,c</sup>	2650							
Secant Modulus, E <sub>50</sub> [MPa]	225 <sup>a,c</sup>	$30^{d}$							
Poisson's Ratio, v	0.32 <sup>b</sup>	0.2							

a) Durham et al. 2003, b) Helgerud et al. 2009, c) Hyodo et al. 2005, d) Yun et al. 2007

#### **MILESTONE LOG**

Milestone	Planed completion date	Actual completion date	Verification method	Comments		
Literature review	5/2013	5/2013	Report	Completed first phase. Will continue throughout the project		
Preliminary laboratory proto- col	8/2013	8/2013	Report (with preliminary val- idation data)	this and previous reports		
Cells for Micro-CT	8/2013	8/2013	Report (with first images)	this and previous reports		
Compilation of CT images: segregated hydrate in clayey sediments	8/2014	Completed Additional tests in progress	Reports (with images)	Given the complexity of hydrate formation in clays, this task continues to explore additional conditions		
Preliminary experimental studies on gas production	12/2014	In progress	Report (with images)			
Analytical/numerical study of 2-media physical properties	5/2015	In progress	Report (with analytical and numerical data)			
Experimental studies on gas production	12/2015		Report (with data)			
Early numerical results related to gas production	5/2016	In progress	Report			
Comprehensive results (in- cludes Implications)	9/2016		Comprehensive Report			

# PRODUCTS

• Publications:

In progress

• Presentations:

In progress

- Website: Publications and key presentations are included in <a href="http://pmrl.ce.gatech.edu/">http://pmrl.ce.gatech.edu/</a> (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: None at this point.

# PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS

*Research Team*: The current team is shown next. We anticipate including external collaborators as the project advances



# IMPACT

While it is still too early to assess impact, we can already highlight preliminary success of exploring hydrate lenses morphology in real systems, and analogue studies using a high resolution tomographer.

# **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: in our academic cycle, higher expenditures typically take place during the summer quarter.

Baseline Reporting Quarter DE-FE009897	Budget Period 1							Budget Period 2									
	Q1		C	Q2 Q3		13	Q4		Q1		Q2		Q3		Q4		
	10/1/12 - 12/31/12		1/1/13 -	1/1/13 - 3/31/13		4/1/13 - 6/30/13 7/1		7/1/13 - 9/30/13		10/1/13 - 12/31/13		1/1/14 - 3/31/14		4/1/14 - 6/30/14		7/1/14 - 9/30/14	
	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total	
Baseline Cost Plan																	
Federal Share	36,664	36,664	36,664	73,327	36,664	109,991	36,664	146,654	38,578	185,232	38,578	223,811	. 38,578	262,389	38,578	300,967	
Non-Federal Share	10,922	10,922	10,922	21,844	10,922	32,765	10,922	43,687	11,250	54,937	11,250	66,186	11,250	77,436	11,250	88,685	
Total Planned	47,585	47,585	47,585	95,171	47,585	142,756	47,585	190,341	49,828	240,169	49,828	289,997	49,828	339,824	49,828	389,652	
Actual Incurred Cost																	
Federal Share	0	0	16,173	16,173	20,191	36,364	66,556	102,920	22,923	125,843	16,448	142,290	89,396	231,686	43,595	275,281	
Non-Federal Share	0	0	52,426	52,426	13,106	65,532	0	65,532	28,443	93,975	28,443	122,418	-45,818	76,600	-1,866	74,735	
Total Incurred Costs			68,600	68,600	33,297	101,897	66,556	168,453	51,366	219,818	44,891	264,709	43,578	308,287	41,729	350,016	
Variance																	
Federal Share	-36,664	-36,664	-20,490	-57,154	-16,473	-73,626	29,893	-43,734	-15,656	-59,389	-22,131	-81,520	50,818	-30,702	5,017	-25,686	
Non-Federal Share	-10,922	-10,922	41,505	30,583	2,184	32,767	-10,922	21,845	17,194	39,039	17,194	56,232	-57,068	-835	-13,115	-13,950	
Total Variance	-47,585	-47,585	21,015	-26,571	-14,289	-40,859	18,971	-21,888	1,538	-20,351	-4,937	- 25, 288	-6,250	-31,537	-8,098	-39,636	

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