

# Oil & Natural Gas Technology

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Quarterly Research Performance Progress Report (Period ending 3/31/2015)

## 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 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:

- New methods for CO<sub>2</sub> hydrate in fine-grained sediments
  - Gas bubble injection into kaolinite slurry
  - Transformation from ice to hydrate in hydrophobic silica
- Process monitoring and X-ray imaging
- Crystallization of different minerals in solution

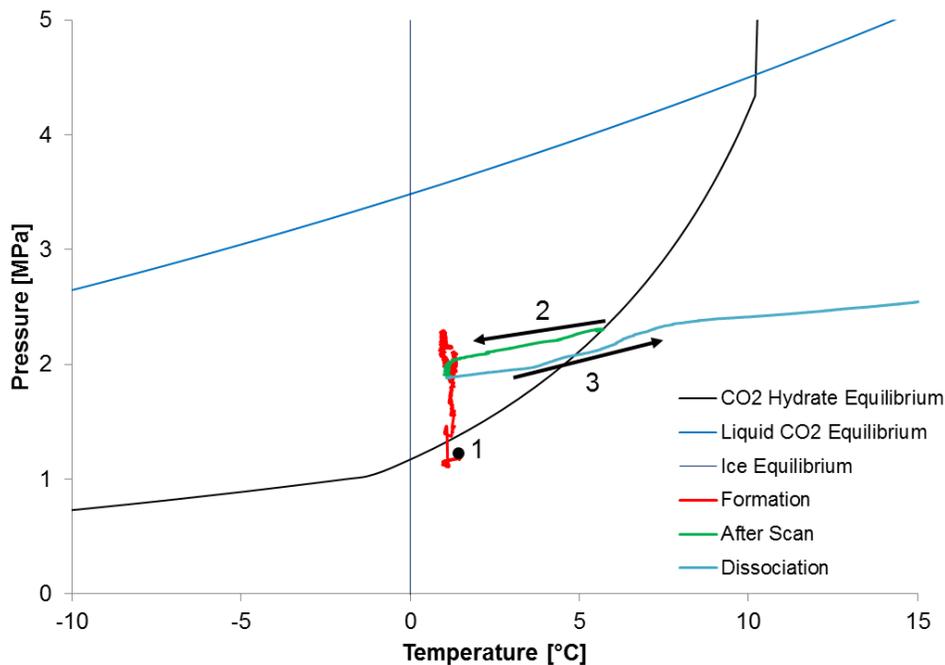
### Plan - Next reporting period

Physical understanding of hydrate formation in pores. Evaluate the difference among gas pressure, liquid pressure and crystal pressure, and their relevance to hydrate stability. Advance numerical model studies of physical properties of hydrate bearing sediments. Well production simulation with numerical methods.

## Research in Progress

### Hydrate formation in very soft clays

A new set of experiments was performed in an attempt to simulate hydrate growth in very soft shallow marine clays. Kaolinite clay slurries (water content 150%) were pressurized with CO<sub>2</sub> to a pressure just below that of hydrate equilibrium. Afterwards, gas was slowly injected from the bottom of the sediment column in the pressure chamber, gradually bringing the system into CO<sub>2</sub> hydrate equilibrium. Specimens were scanned at multiple stages. Thin hydrate veins formed at the base of sediment column near the injection point. Gas bubbles trapped in the sediment developed a hydrate shell along gas-sediment interface.



Pressure-Temperature evolution. 1) start of experiment (specimen pressurized to 1.1 MPa inside of the cooling chamber), 2) During scanning, the chamber warms up and reaches the hydrate equilibrium phase boundary (no data during scanning), 3) Warming dissociation path.

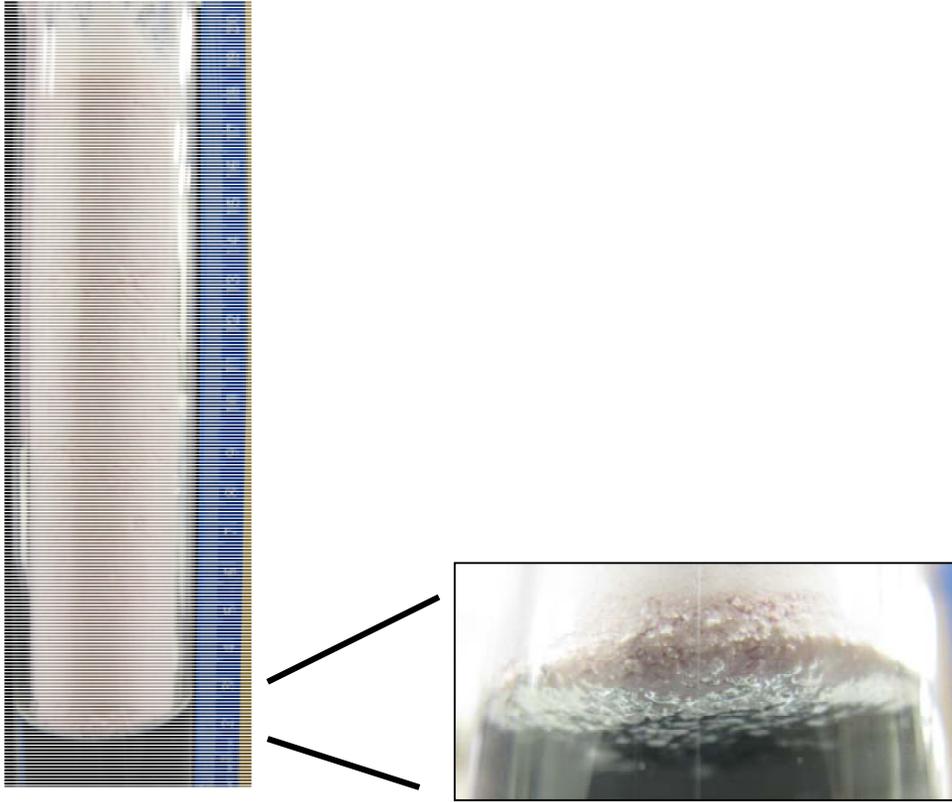


X-ray slices after hydrate formation. Color code: black= CO<sub>2</sub> gas; blue= hydrate; green= water saturated kaolin; yellow= aluminum chamber

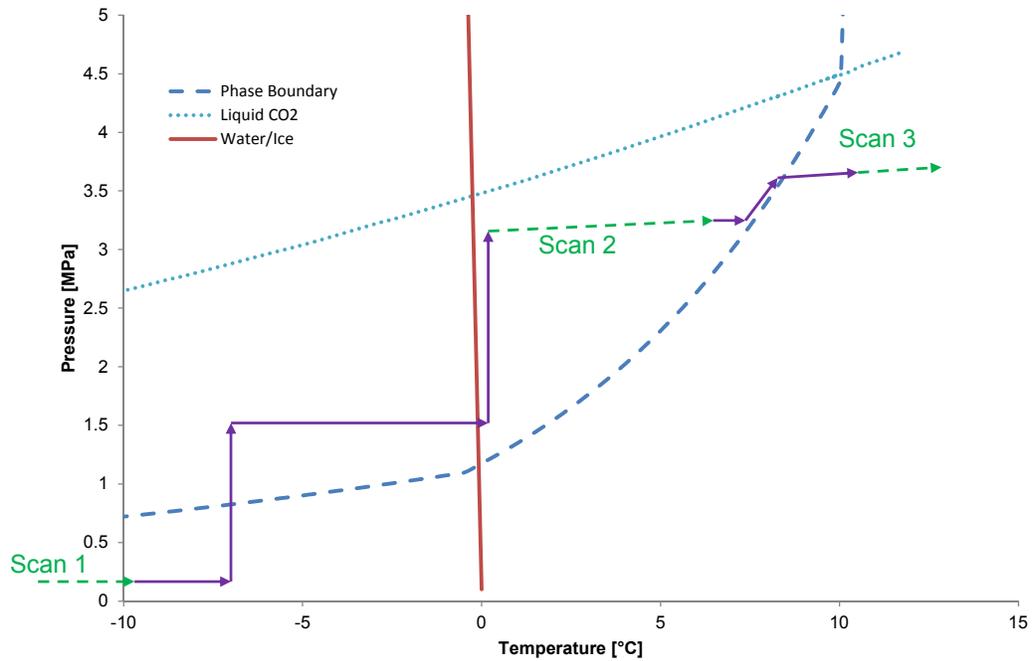
### **Ice-to-hydrate transformation in hydrophobic silica**

High contact angle hinders water migration and a different hydrate morphology is expected in hydrophobic sediments than in hydrophilic specimens (surface-level studies reported in Jong and Santamarina – Previous results with ice-hydrate transformation in hydrophilic sediments have been reported earlier as part of this project).

In this study, we used hydrophobic silica flour that has been pretreated with chlorosilanes. The photo on the left shows a column of hydrophobic silica powder floating on top of water. Images on the right show a detailed look at the interface between the powder and water.



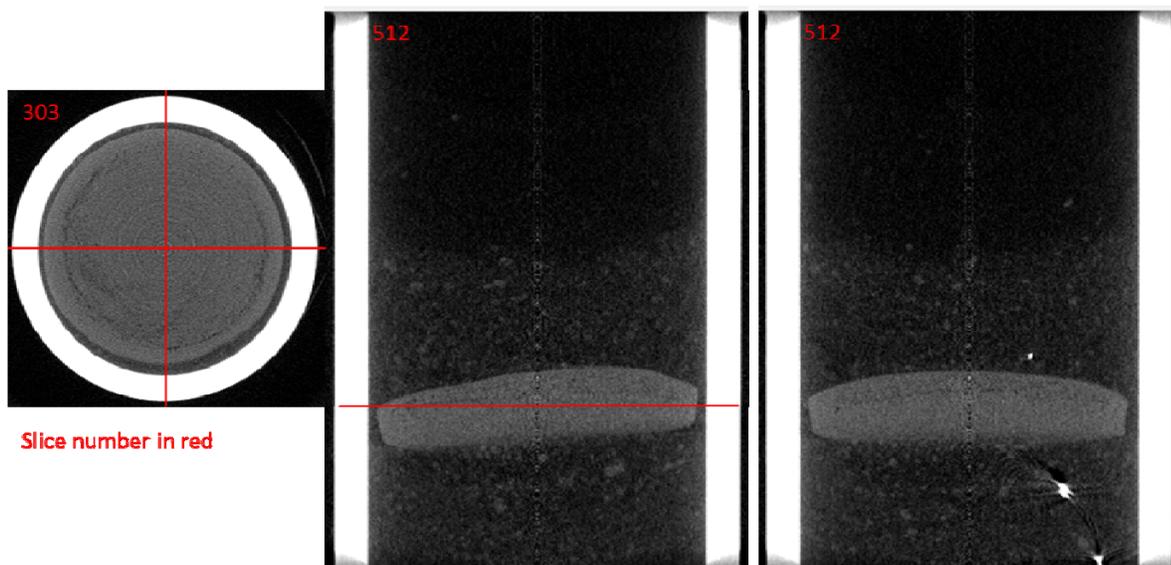
Several tests were conducted as part of this series. The target pressure-temperature trajectory is schematically shown below. Once pressurized, specimens are kept at constant mass. Measured PT paths show increased temperature and decreased pressure as gas is consumed during the exothermic process which starts before the ice-water phase boundary, clearly seen starting at around  $-1^{\circ}\text{C}$ .



Scans for two experiments are shown next, whereby different size ice-lenses were buried in the pre-cooled hydrophobic silica flour.

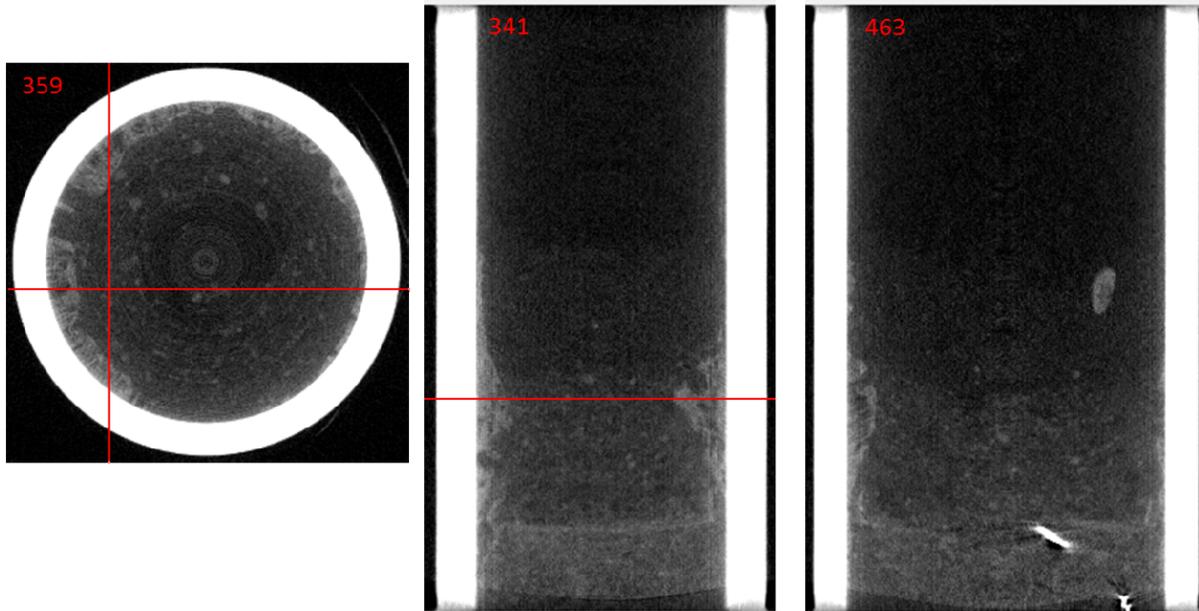
Test with one lens

Initial condition – Scan 1

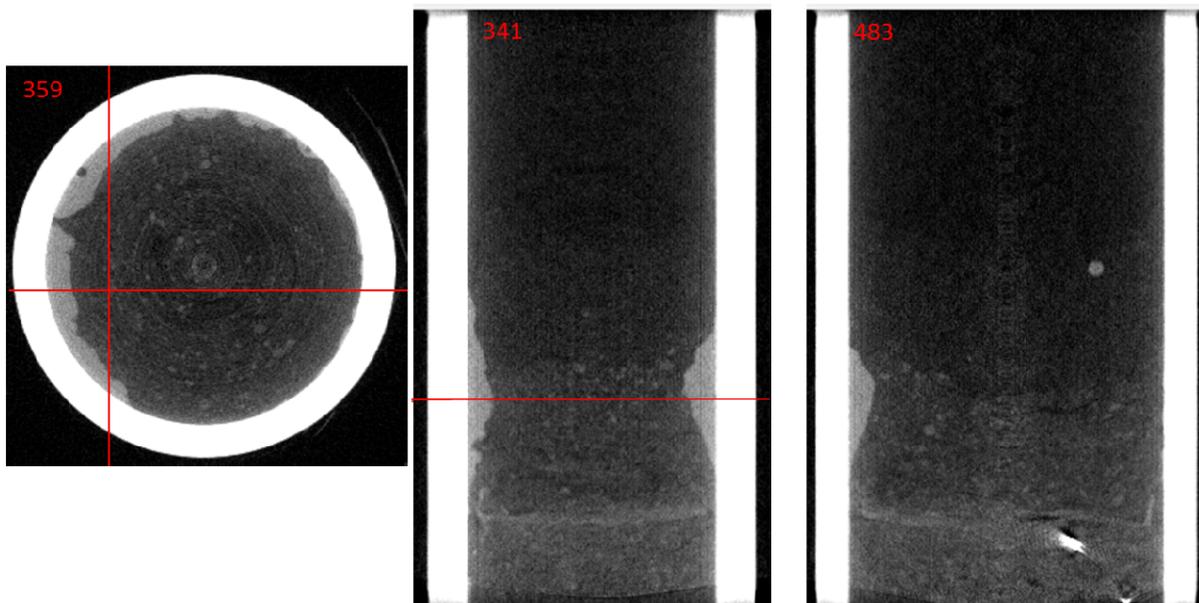


Slice number in red

After hydrate formation – **Scan 2** – Notice the porous hydrate structure and its preferential distribution on the hydrophilic aluminum wall along the periphery.



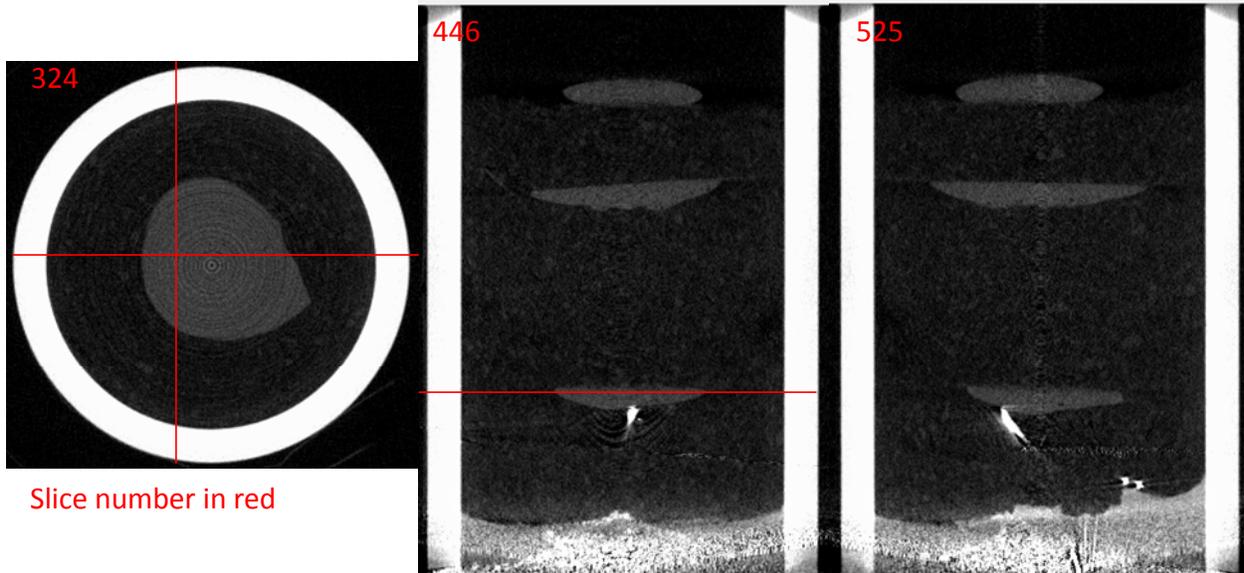
After hydrate dissociation – **Scan 3**



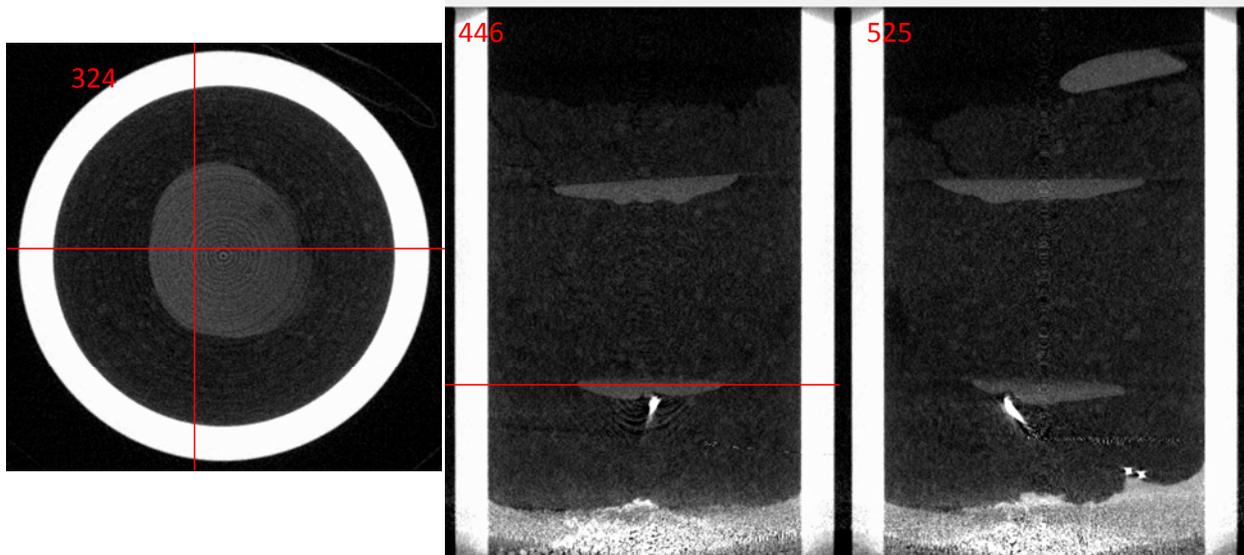
Test with three lenses

Three small ice lenses are buried within the hydrophobic silica flour, away from the aluminum wall.

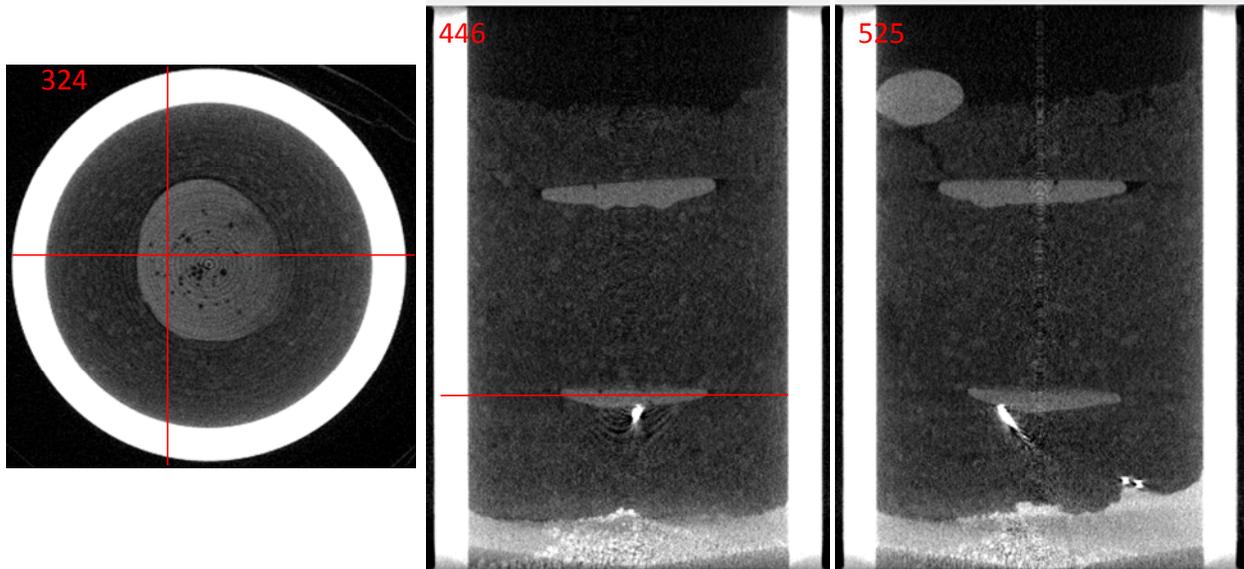
Initial condition – Scan 1



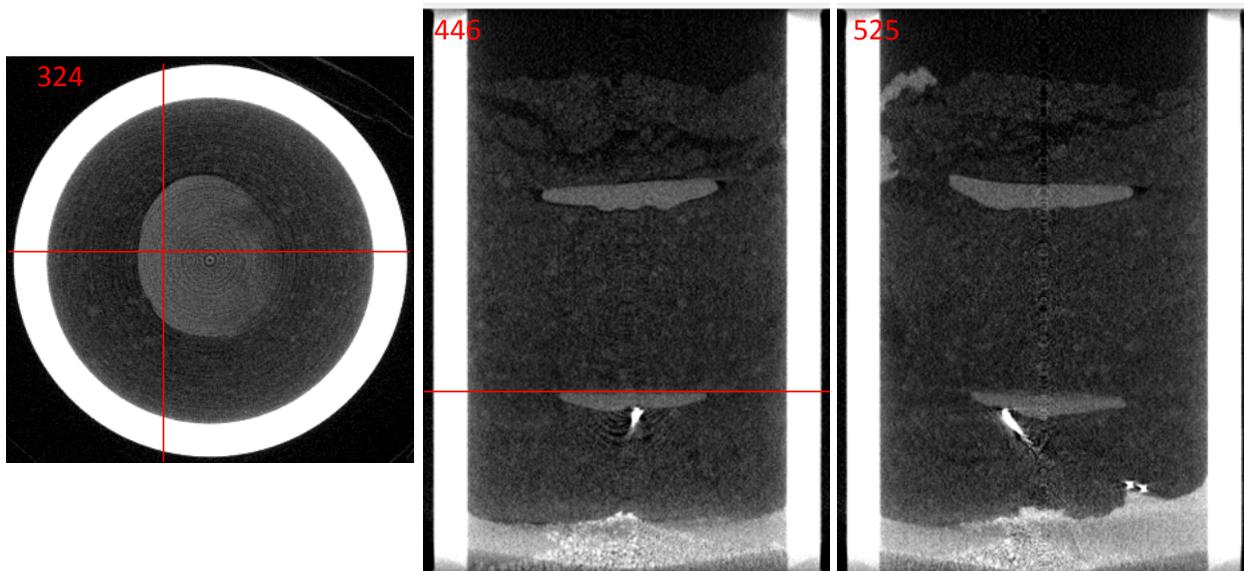
After hydrate formation – Scan 2. Note sediment fractures, upper lense migration (potential vibration or gas release)



After hydrate dissociation – Scan 3. The top water droplet rotates downwards and exhibits high contact angle.



After hydrate reformation from water – Scan 4 (once again, preferential growth along hydrophilic wall)



## MILESTONE LOG

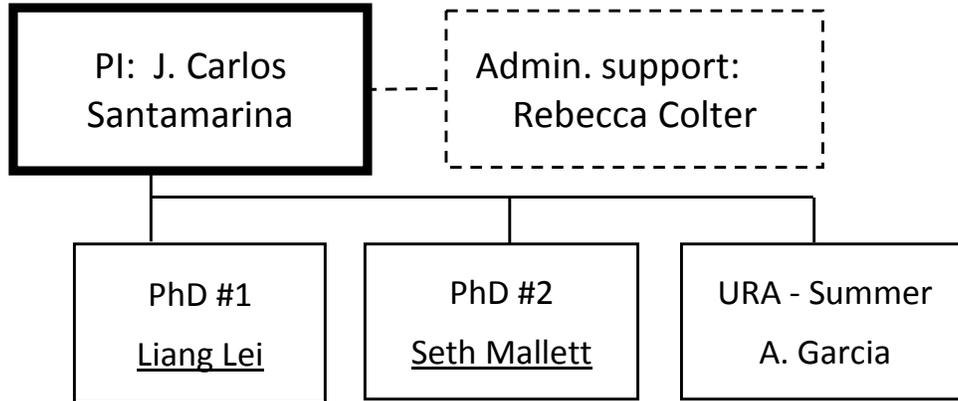
Milestone	Planned completion date	Actual completion date	Verification method	Comments
Literature review	5/2013	5/2013	Report	Completed first phase. Will continue throughout the project
Preliminary laboratory protocol	8/2013	8/2013	Report (with preliminary validation data)	this and previous reports
Cells 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	Continued progress	Report (with images)	this and previous reports
Preliminary experimental studies on gas production	12/2014	12/2014	Report (with images)	Jang's thesis
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			
Early numerical results related to gas production	5/2016	In progress	Report	
Comprehensive results (includes Implications)	9/2016		Comprehensive Report	

## PRODUCTS

- **Publications:**  
In progress
- **Presentations:**  
In progress
- **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:** 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 3					
	Q2		Q3		Q4	
	1/1/15 - 3/31/15		4/1/15 - 6/30/15		7/1/15 - 9/30/15	
	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total
<b>Baseline Cost Plan</b>						
Federal Share	40,059	381,086	40,059	421,145	40,059	461,204
Non-Federal Share	11,587	111,860	11,587	123,447	11,587	135,034
Total Planned	51,647	492,945	51,647	544,592	51,647	596,238
<b>Actual Incurred Cost</b>						
Federal Share	56,843	389,933				
Non-Federal Share	36,582	137,278				
Total Incurred Costs	93,425	527,211				
<b>Variance</b>						
Federal Share	16,784	8,848				
Non-Federal Share	24,995	25,419				
Total Variance	41,779	34,266				

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