Oil & Natural Gas Technology

DOE Award No.: DE-FE0009897

Quarterly Research Performance Progress Report (Period ending 9/30/2015)

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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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:

- Solubility of various gases in water – potential new analogs for hydrate in fine-grained sediment
  - High solubility gases, solubility of noble gas
  - Hydrate stability boundaries of Xenon hydrate and CO_2 hydrate with promoters
- Formation of CO_2 hydrate in fine-grained sediments
  - Bubbling in kaolinite slurry
- Formation of THF hydrate in different types of fine-grained sediments
- Topology of gas hydrate in fine-grained sediments study

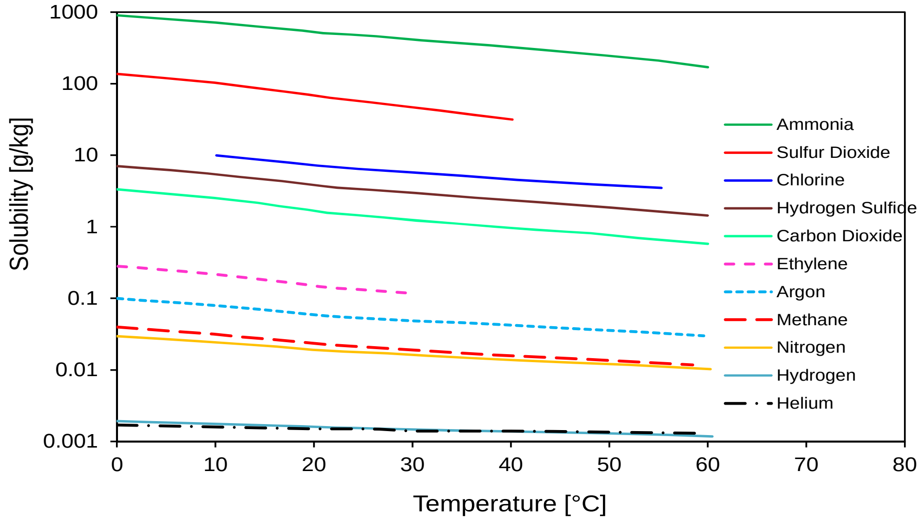
Plan - Next reporting period

Compile available X-ray images of pressure cores with segregated hydrate formation. Quantitative analysis of hydrae lenses topology in fine-grained sediments. Physically evaluate the factors that influence the topology of natural crystals. Advance numerical model studies of physical properties of hydrate bearing sediments based on new findings in topology. Chemophysical understanding of CO_2 hydrate formation promoters (e.g., cyclopentane, tetra-*n*-butyl ammonium bromide/chloride/fluoride).

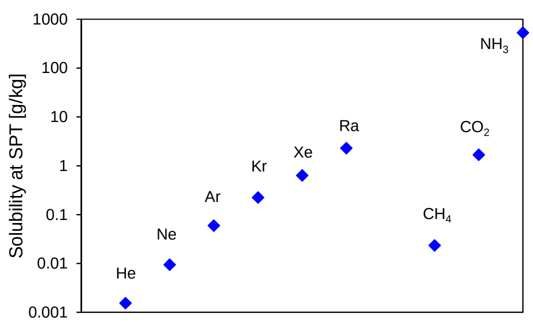
Research in Progress

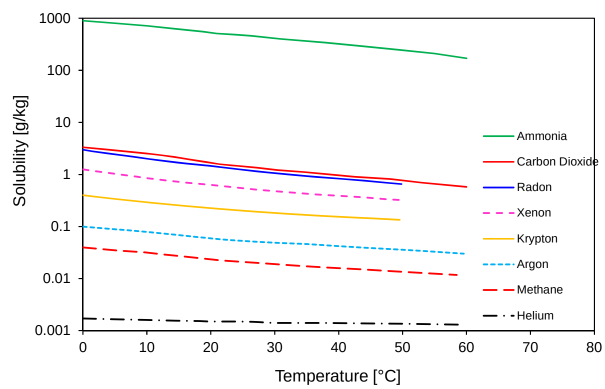
Gas solubility in water – Nobel gases

Hydrate crystal growth in fine-grained sediment is inhibited by the low solubility of hydrate former gas. The solubility of different gases in water may vary six orders of magnitude in water at identical pressure/temperature conditions.

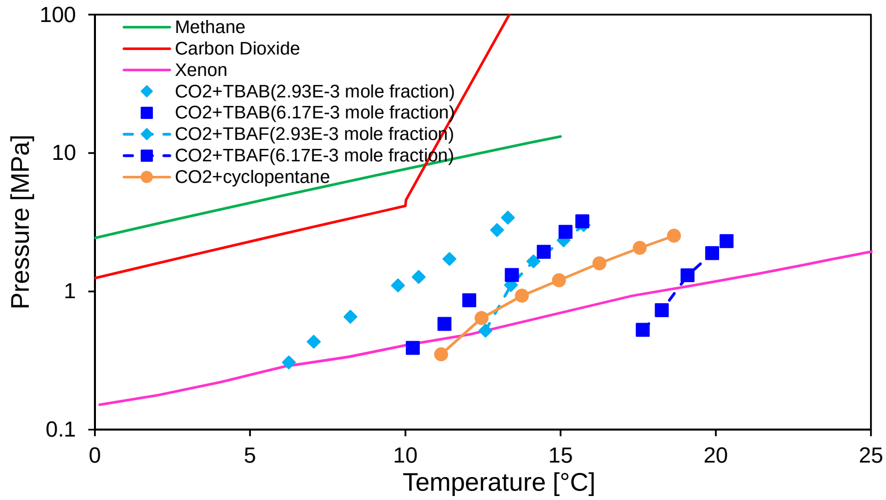


At standard pressure-temperature conditions, Argon, Krypton, Xenon, and Radon have higher solubility in water than that of methane gas. Other advantages of using noble gases as hydrate former include (1) high attenuation of X-ray intensity so that noble gas hydrate can be easily distinguished in CT images, and (2) much lower hydrate stability boundaries than that of methane and CO_2 hydrate.



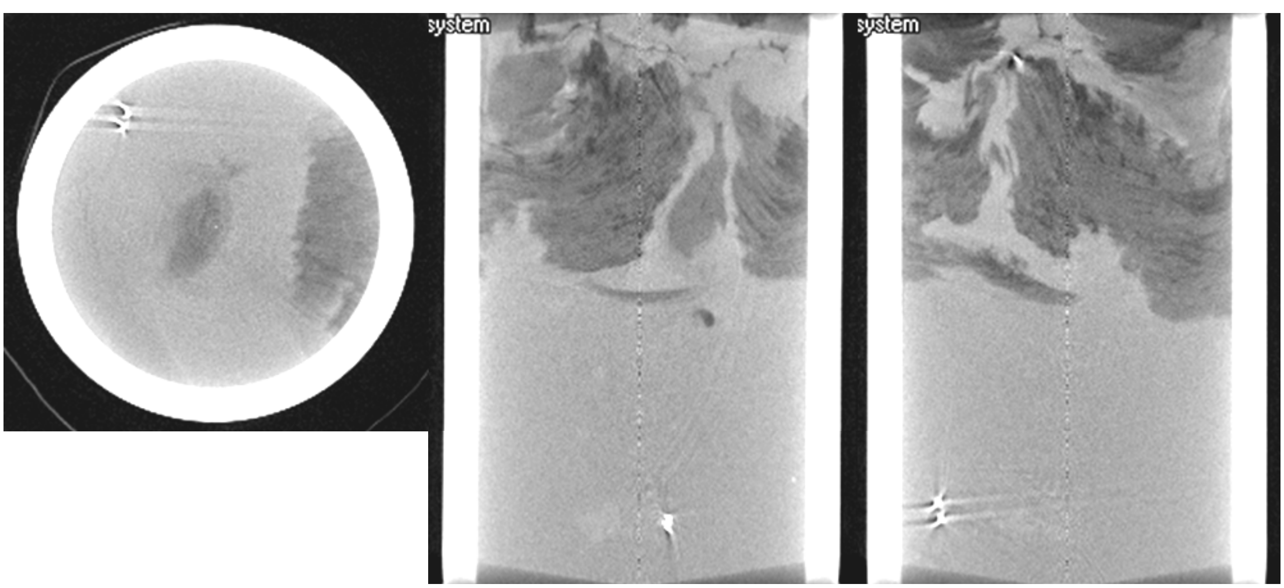


The stability boundary for carbon dioxide hydrate can be lowered dramatically by adding tetra-*n*-butyl ammonium bromide salts or cyclopentane. Xenon gas hydrate can form under ~1MPa pressure at room temperature (20°C). Thus, current testing conditions (i.e., 10MPa pressure and 4°C) can create much higher nucleation driving force for Xenon and carbon dioxide (with formation promoters) hydrate.

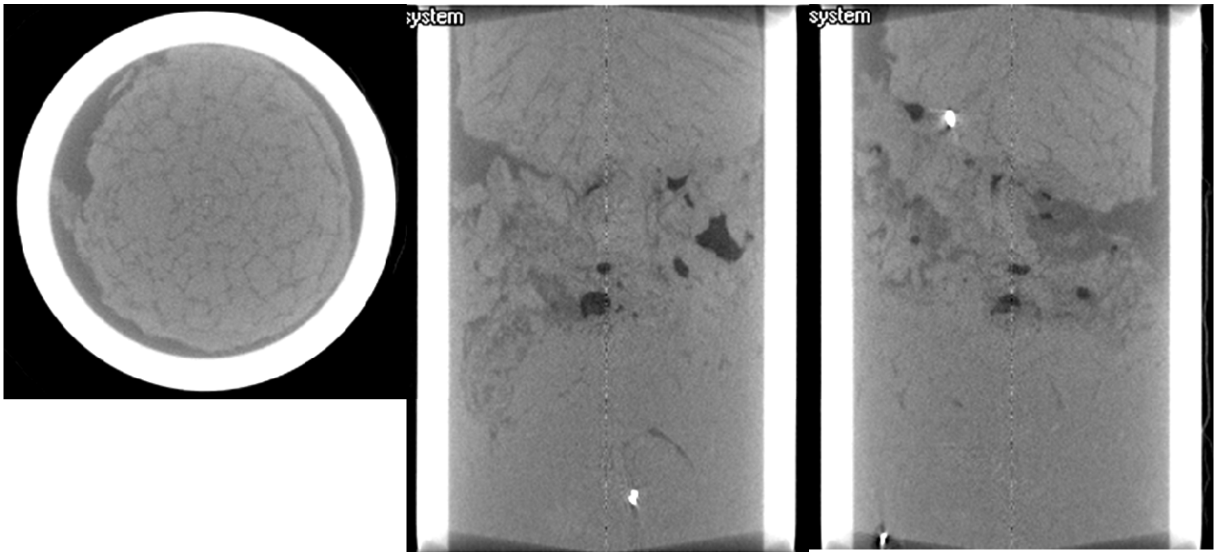


Gas bubbling into kaolinite slurry to form CO_2 hydrate

CO_2 gas bubbles were injected into kaolinite slurry from the bottom of the chamber, with a controlled rate. The X-ray image after gas injection follows. Notice the porous structure of massive hydrate.

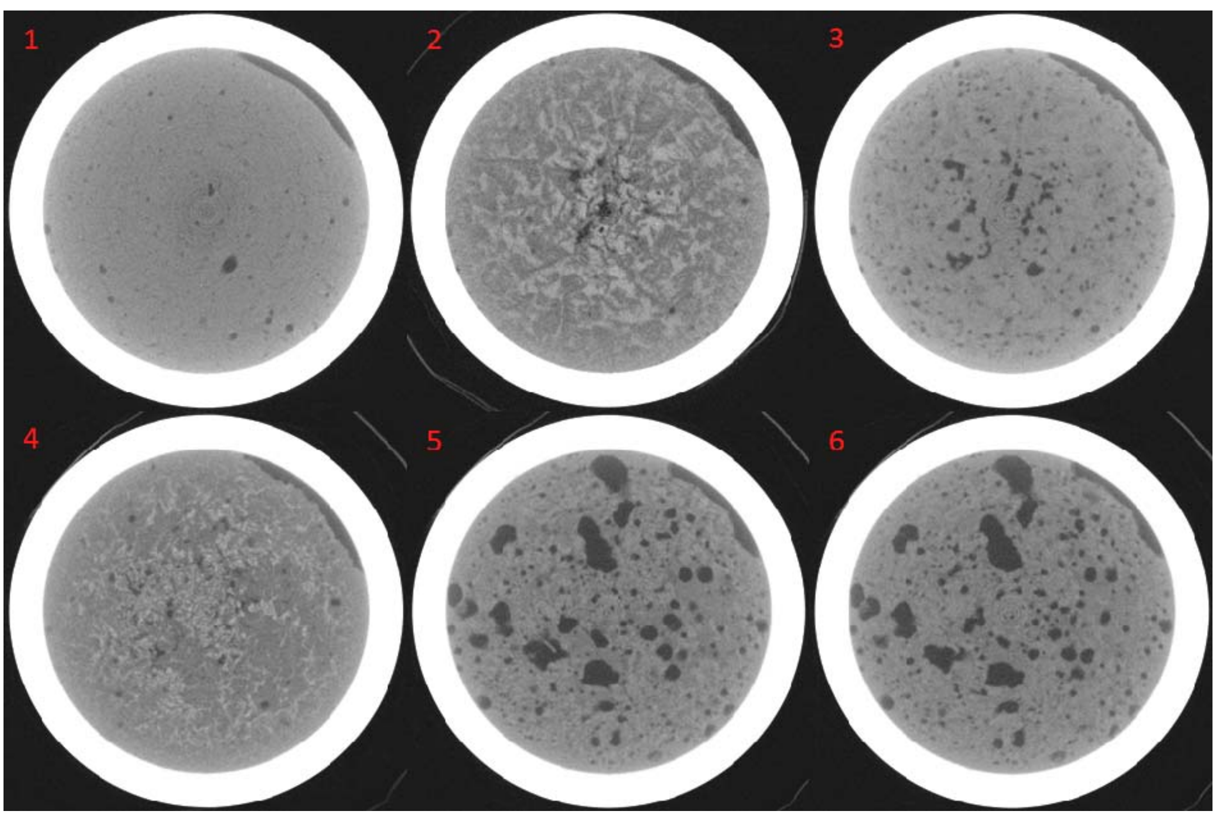


The X ray image after dissociation and re-formation cycle follows. The image on the left shows the polygonal structure of CO_2 hydrate lens formed from dissolved gas.



<u>THF hydrate topology in different types of fine-grained sediments</u>

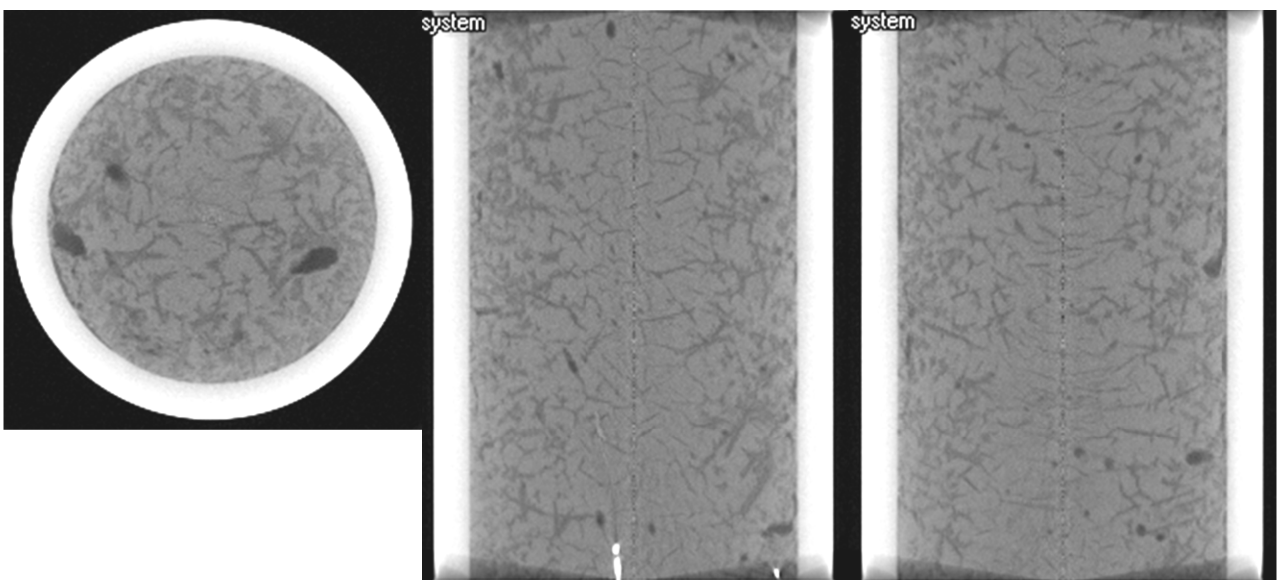
Bentonite:



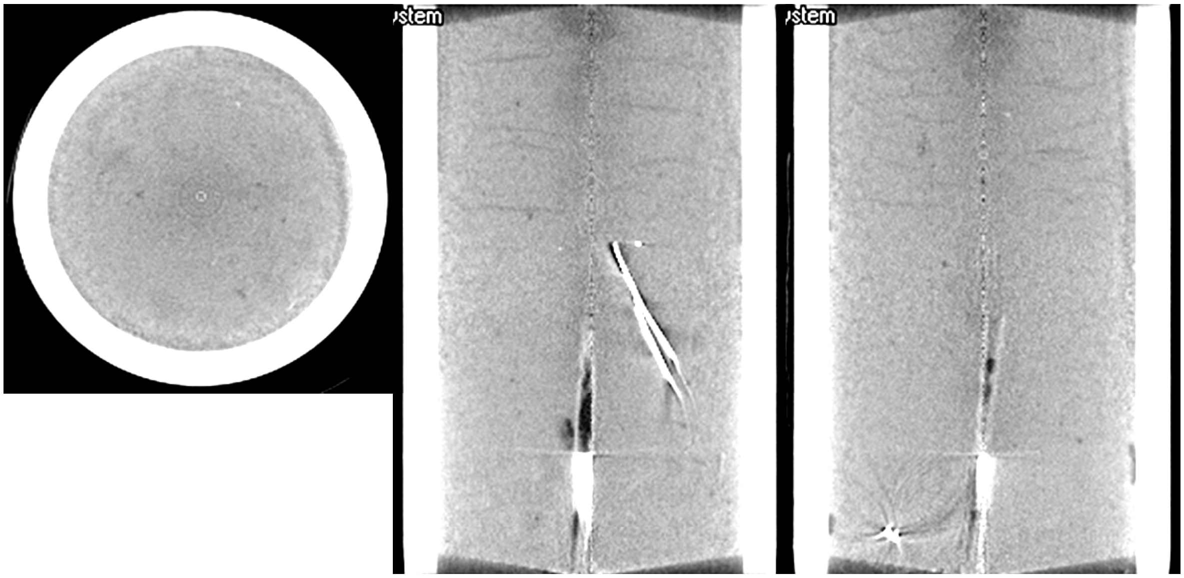
The X-ray image sequence above shows (1) the initial stage, (2) hydrate formation at 2°C (Note that the segregated bright parts are consolidated bentonite), (3) dissociated specimen, (4) hydrate and ice formation at -20°C, finally (5 and 6) show cross sections of the specimen one hour and one day after dissociation.

Hydrate (or ice) formation excludes impurities including ions and non-hydrate forming gas molecules (see segregated gas bubbles in picture 2). The unevenly distributed hydrate mass shows the influence of thermal boundary in hydrate growth, followed by the controlling effect of the changing stress field.

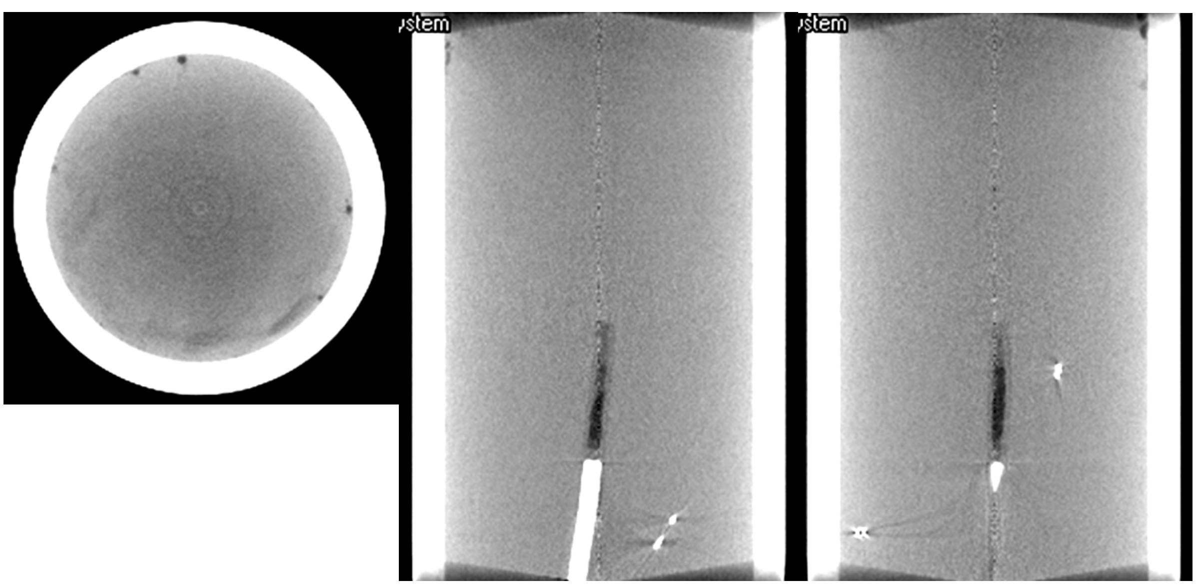
Kaolinite. Once again, hydrate topology reflects thermal boundary and stress-field effects.



Diatomaceous earth: Hydrate forms around the periphery (irregular), and some lenses form in the center of the specimen. The fraction of segregated hydrate decreases with the increase in effective stress, i.e., specimen depth.



Silica flour: For comparison, solid silica flour particles are of the same size as porous diatom grains. Segregated hydrate is observed only at the top of the specimen. The duration of the thermal spike during phase transformation is much shorter in silica flour than in diatomaceous earth (possibly the effect of location relative to nucleation sites).



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	In progress	Report (with images)	
Preliminary experimental studies on gas production	12/2014		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

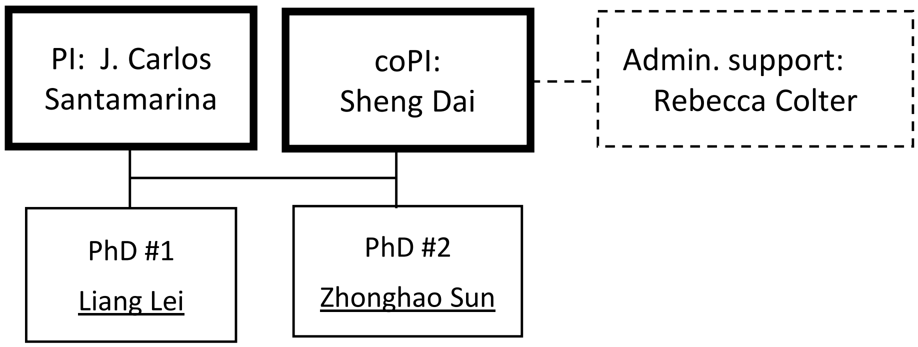
- **Presentations:**

  In progress

- **Website:** Publications and key presentations are included in http://pmrl.ce.gatech.edu/ (for academic purposes only)
- **Technologies or techniques:** X-ray tomographer, X-ray transparent pressure vessel, novel hydrate formation strategies, formation and imaging advantages in noble gasses.
- **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. *Note: As agreed with DOE, Georgia Tech professor Sheng DAI has joined the project.*



IMPACT

Hydrate formation in fine grained sediments (multiple conditions/methods), hydrate topology, hydrate bearing sediment properties, 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; however, most of our charges this summer were minimal as Santamarina and one of the PhDs are not charged to this account any longer even though he remains fully involved in the project. This situation has now been regularized as the new Georgia Tech professor Sheng DAI has joined the project.

Baseline Reporting Quarter DE-FE0013961	Budget Period 2							
	Q1		Q2		Q3		Q4	
	10/1/14 - 12/31/14		1/1/15 - 3/31/15		4/1/15 - 6/30/15		7/1/15 - 9/30/15	
	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total
Baseline Cost Plan								
Federal Share	30,000	168,944	30,000	198,944	30,000	228,944	86,571	315,515
Non-Federal Share	10,495	50,475	10,495	60,970	10,495	71,465	10,945	82,410
Total Planned	40,495	219,419	40,495	259,914	40,495	300,409	97,516	397,925
Actual Incurred Cost								
Federal Share	64,746	186,648	38,605	225,253	19,041	244,294	-	244,294
Non-Federal Share	10,601	50,580	27,525	78,105	-	78,105	-	78,105
Total Incurred Costs	75,347	237,228	66,130	303,358	19,041	322,399	-	322,399
Variance								
Federal Share	34,746	17,704	8,605	26,309	-10,959	15,350	-86,571	-71,221
Non-Federal Share	106	105	17,030	17,135	-10,495	6,640	-10,945	-4,305
Total Variance	34,852	17,809	25,635	43,444	-21,454	21,990	-97,516	-75,526

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