Oil & Natural Gas Technology

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Quarterly Research Performance Progress Report (Period ending 3/31/2013)

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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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 first period include:

- Training of the two new PhD Students that form the team on different aspects central to the project
    - hydrates and hydrate bearing sediments
    - formation, properties, characterization
    - high pressure devices and analytical tools (including gas chromatography)
- Continued literature review and analyses
    - hydrate morphology in fine grained sediments based on in situ and pressure core-based observations
    - phase boundaries for stable/efficient exchange
- Imaging studies
    - system design for high resolution CAT scan tomographer
    - preliminary testing of components
- Preliminary study of gas replacement as a potential production mechanism to reduce reservoir deformations and premature closure

Plan - Next reporting period

We move back to our rebuilt laboratory in July. The new facility will house our new imaging capabilities currently under development. As we optimize the potential of the new facility for this project, the goals for this quarter are to advance all experimental procedures related to hydrate formation in clays and X-ray imaging for process monitoring.

Research in Progress

Clayey sediments, in particular those with charged interlayers affect the behavior of methane hydrates within the interlayer and may inhibit both methane hydrate nucleation and growth. Hydrate formation within charged interlayers and the ensuing capillary pressure disturbs the hydrate phase-equilibrium.

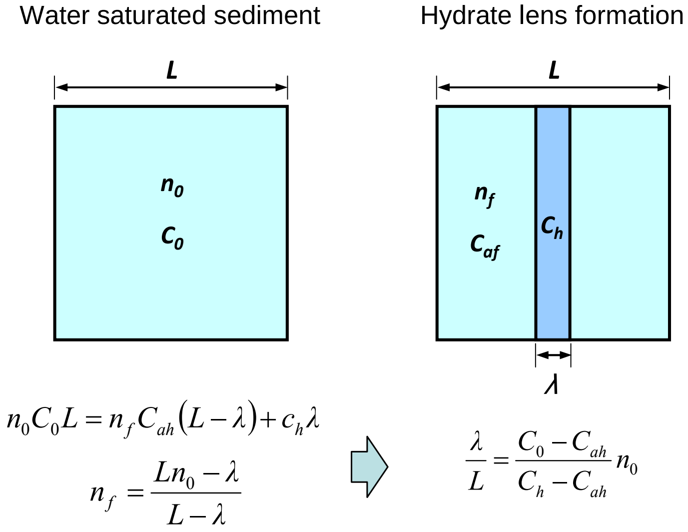
The pressure and temperature *P-T* dependent concentration of a certain species in another component $M_{P,T}$ [mol/m^3] can be approximated using Henry's law as a linear function of pressure

$$M_{P,T} = P_{applied}\, k_H^0 \cdot \exp\left[\frac{-\Delta H}{\underline{R}}\left(\frac{1}{T} - \frac{1}{298.15K}\right)\right]$$

where the enthalpy of the solution is ΔH=-14130 [J/mol] for CH_4 in water and ΔH=-19940 [J/mol] for CO_2 in water, Henry's law constant at 298.15 [K] is $k_H^o=1.3\times10^{-3}$ [M/atm] for methane and $k_H^o=3.4\times10^{-2}$ [M/atm] for carbon dioxide [Wilhelm et al., 1977; Osegovic et al., 2006], and the universal gas constant is R=8.314 [J/(mol·K)]. Hence, the solubility of gas in water increases with increasing pressure and decreasing temperature outside the hydrate stability *P-T* conditions.

Solubility is affected by the presence of other phases or competing solutes. For example, the presence of hydrates facilitates further hydrate formation and the equilibrium concentration of gas in water decreases. The gas solubility trend with respect to pressure and temperature is also altered by the presence of hydrate. Within the hydrate stability field, a temperature decrease under constant pressure or a pressure increase at constant temperature forces methane molecules in the liquid water to form more hydrate, which reduces the gas solubility in water. Salt is a competing solute for dissolved gas and therefore lowers the solubility of gas in water.

The solubility dependence on pressure, temperature, and the presence of hydrate can cause unique phenomena during hydrate formation (details in an upcoming manuscript by Jang and Santamarina). Consider a sediment of initial porosity n_o and a pore water gas concentration C_o surrounded by a closed boundary, i.e., constant mass (see figure). Let's assume that a hydrate lens forms using the excess gas dissolved in the pore water. The hydrate lens thickness is calculated using the saturated gas concentration in the absence of hydrate C_o, the gas solubility in the presence of hydrate C_{ah}, gas concentration in hydrate C_h and the initial sediment porosity n_0.



$$n_0 C_0 L = n_f C_{ah}(L-\lambda) + c_h \lambda$$

$$n_f = \frac{L n_0 - \lambda}{L-\lambda}$$

$$\frac{\lambda}{L} = \frac{C_0 - C_{ah}}{C_h - C_{ah}} n_0$$

Figure 1. Thickness of a hydrate lens that could form from the initially dissolved excess gas. Hydrate lens thickness λ in a medium with lens-to-lens spacing L is a function of the initial porosity n_0, gas solubility in the absence and in the presence of gas hydrate c_0 and c_f, and gas concentration in hydrate c_h.

$$\frac{\lambda}{L} = \frac{C_0 - C_{ah}}{C_h - C_{ah}} n_0 \qquad \text{Hydrate lens thickness}$$

For example, a hydrate lens thickness of λ=4mm is anticipated for lenses separated by L=1m in a sediment with an initial porosity n_o=0.4 if the initial methane concentration is C_0=0.14mol/kg (P=12MPa and T=288K), when the methane solubility in the presence of hydrate is C_{ah}=0.063mol/kg, given that the methane concentration in hydrate is C_h=8.06mol/kg (see values in Table 4.1 when P=6.6MPa and T=274K).

Porosity decreases in the sediment surrounding the lens; invoking mass conservation once again,

$$n_f = \frac{n_0 - \lambda/L}{1 - \lambda/L}$$

Further lens growth requires additional water and gas transport to the size and tip of lenses. The thin fluid layer between grains and hydrates, known as pre-melted films, may facilitate transport. In fact, these films are used to explain ice lens formation in frozen ground. However, they hypothesis of pre-melted films as preferential paths for gas diffusion and water supply requires further study.

On the other hand, the mechanical interaction between lenses and the surrounding sediment is now well understood (published fundamental studies by Shin and Santamarina). Nearby lenses interact through the effective stress field (in the absence of additional gradients, such as geothermal), and leads to lenses intersections resulting in interconnectivity. Ice lense rotation due to the stress field is captured in the following tomogram

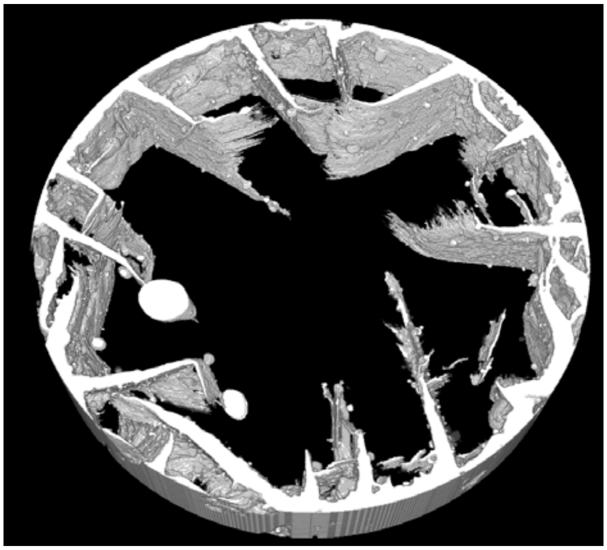


Figure 2. Ice lens rotation due to effective stress field – (obtained using the microtomographer at Grenoble – France)

If hydrate lenses were isolated, lens growth would be limited by gas diffusion across the sediment. However, lens intersection/interconnectivity and the presence of potentially effective conduction paths described above may explain the complex topologies inferred from logging and observed in pressure cores (see Figures 3 and 4).

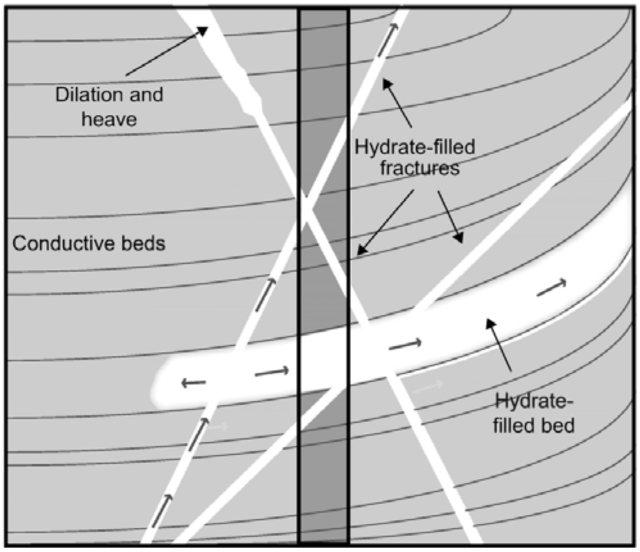


Figure 3. Lenses topology (Cook, Goldberg, & Kleinberg, 2008)

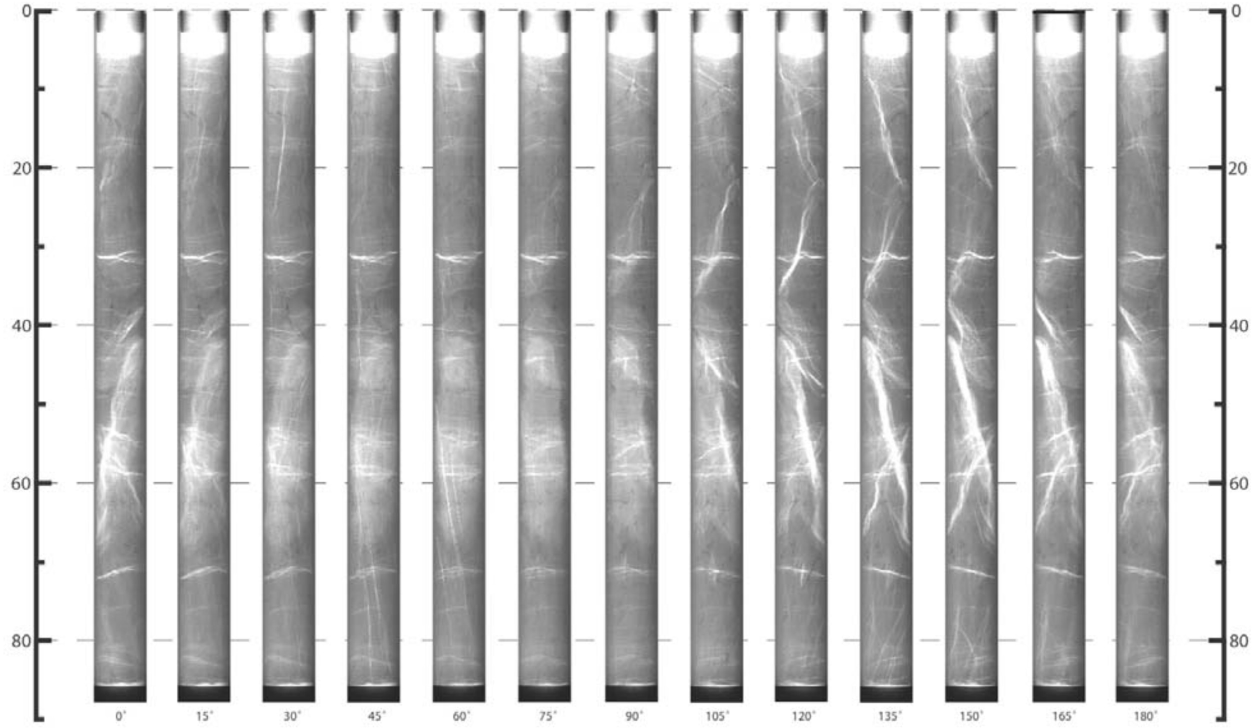


Figure 4. X-ray results of hydrate lens topology (Cook, 2010)

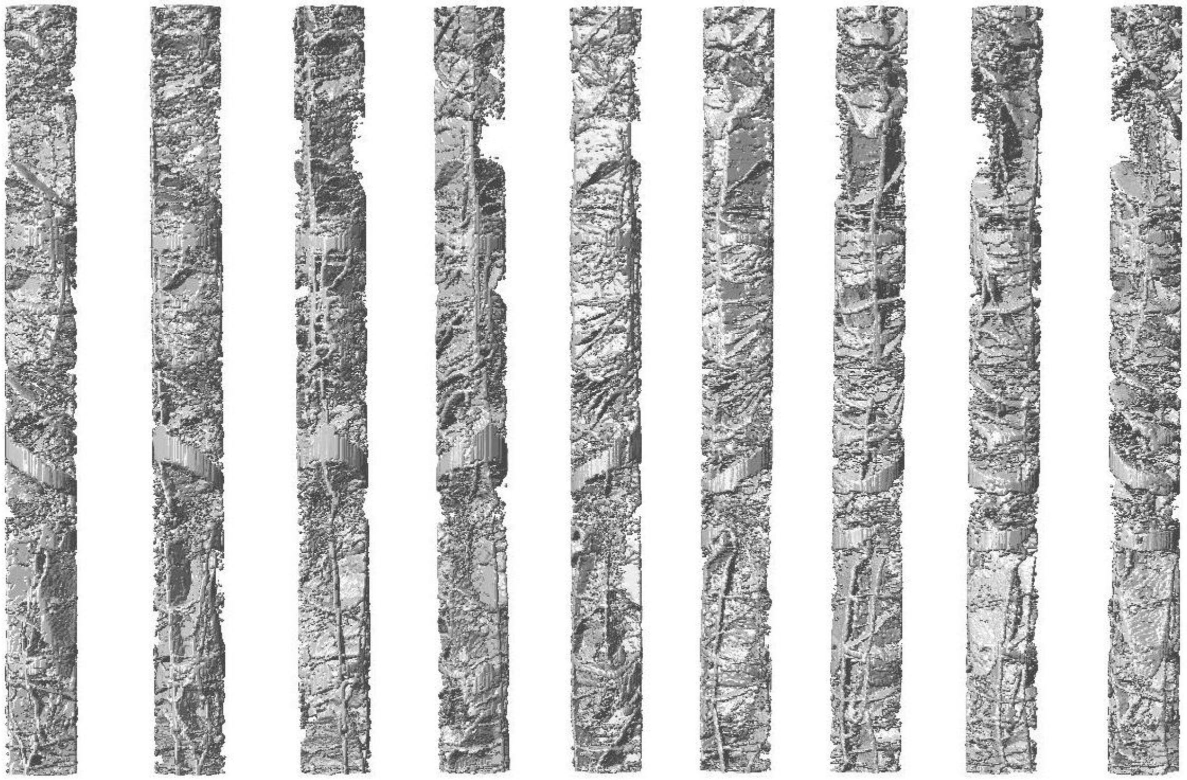


Figure 5. Hydrate topology (South Korea). Tomographic views obtained for different rotations (post processed - from Geoteck's data)

The CO_2 molecule can replace the CH_4 molecule within the larger cages; the heat released in this exchange can sustain the reaction. The addition of nitrogen along with carbon dioxide, promotes further exchange where by the smaller nitrogen molecule can replace methane in the smaller cages increasing methane production from 64% to 85%. Most importantly for this project, permeability shut-off during depressurization and volume contraction can be mitigated with a combination of gas exchange, thermal stimulation and proper pressure control.

Hydrate topoloy studies and potential mixed-mode gas production strategies have stimulated new laboratory improvements including gas chromatography and x-ray imaging/microtomography. Gas chromatography has been added within our fluid pressure/volume control system (Figure 6). Calibrations for different conditions are underway.

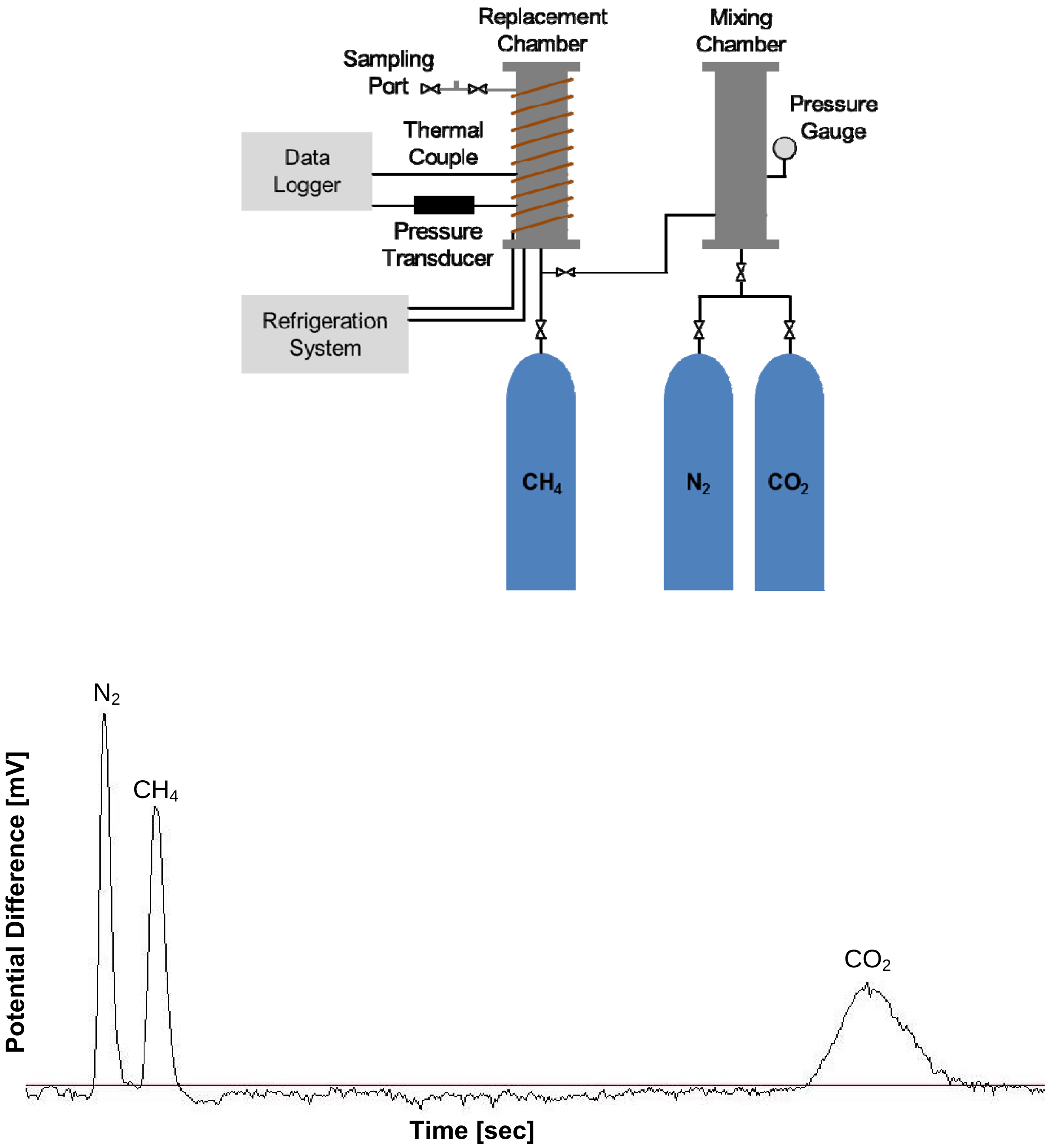


Figure 6. Equipment schematic and sample chromatogram for a CH4, N2, and CO2 replacement study.

The development of a versatile x-ray microtomography system for this project has involved the selection of the five main components: source, detector, specimen positioning mechanism, reconstructive software, and safety features/shield. We are making these choices with advice from D. Goldman (Physics), N. Zakir (Radiation Safety Officer, GT), P. Schultheiss (Geotek), and vendors of components and devices.

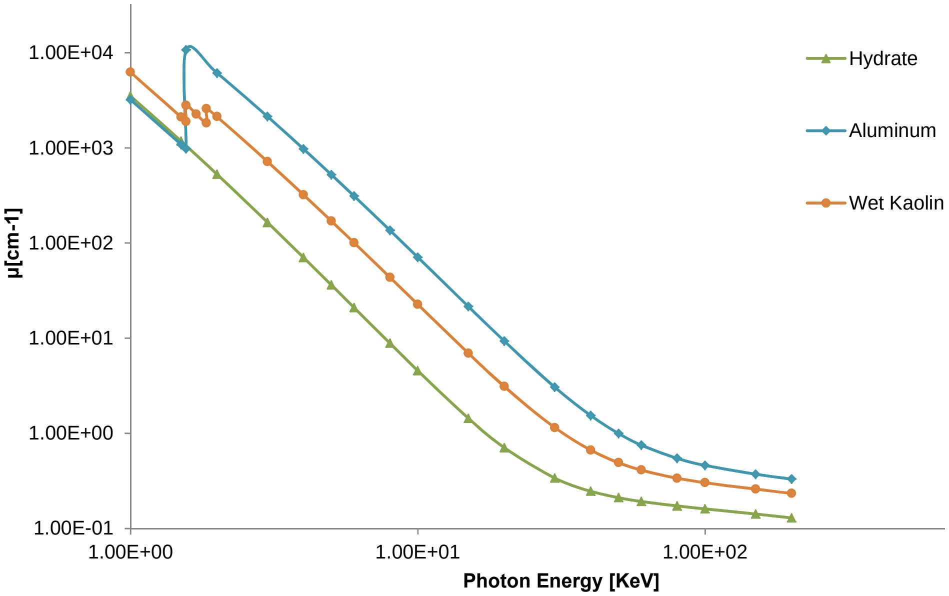


Figure 7. Linear attenuation coefficients of hydrate and clay within an aluminum casing.

The most important considerations in selecting the x-ray detector have involved: the dynamic ratio (the ratio between the highest and lowest detected values), the field of view (FOV), sensitivity (ability to detect low energy x-rays), pixel number, spatial resolution, and scintillator material. The open-source OSCaR, software will be used for reconstruction (3D cone-beam tomography - Feldkamp-Davis-Kreiss FDK algorithm).

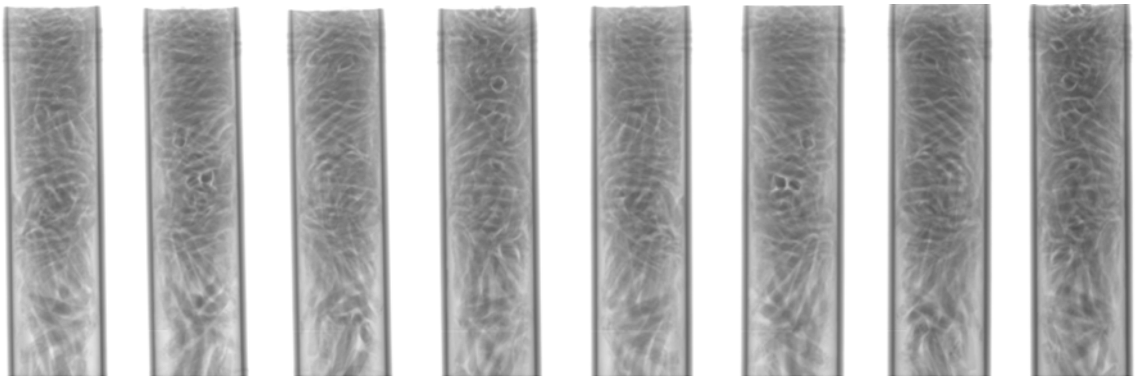


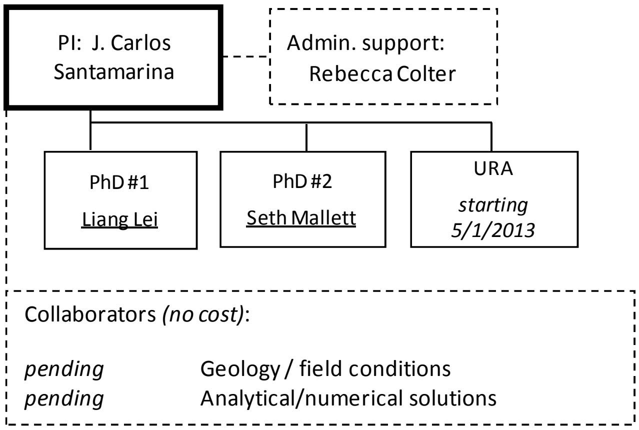
Figure 8. Preliminary testing of potential components. Frozen clayey sediment in aluminum chamber - Stacked projections gathered during continuous rotation (8 turns). 2007 Hamamatsu L9631 microfocus source and Canon CXDI-50G Flat Panel Detector.

PRODUCTS

- **Publications – Presentations:** None at this point
- **Website:** Publications (for academic purposes only) and key presentations are included in http://pmrl.ce.gatech.edu/.
- **Technologies or techniques:** None at this point.
- **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 so far.

SPECIAL REPORTING REQUIREMENTS:

We are progressing towards the required check point on the ability to obtain high resolution images of hydrate bearing clayey sediments.

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