Oil & Natural Gas Technology

DOE Award No.: FWP ESD12011

Status Update
(Period Ending April 30, 2016)

Properties of sediments containing methane hydrate, water, and gas subjected to changing gas compositions

Project Period (October 2015 – April 2016)

Submitted by:
Timothy J. Kneafsey

Signature

Lawrence Berkeley National Laboratory
1 Cyclotron Road
Berkeley, CA 94720
e-mail: tjkneafsey@lbl.gov
Phone number: (510) 486-4414

Prepared for:
United States Department of Energy
National Energy Technology Laboratory

June 13, 2016

Office of Fossil Energy

FWP ESD12011 - Properties of sediments containing methane hydrate, water, and gas subjected to changing gas compositions
Status Update
June 13, 2016
(Text in smaller font was previously submitted but provides background)

Task 7.0 Grain-scale Computation of Hydrate-Bearing Sand Properties Based on microCT Sample Description (collaboration with NETL)

The goal of this task is to evaluate the mechanical impact of different hydrate cementation "motifs" (habits) using realistic starting microstructures, consistent 3D image processing, and accurate 3D Finite Element Models (FEM) to compute key material properties, mainly bulk and shear moduli. To date, we have made significant progress on several components of this task. Previously we reported on acquisition of a 3D microCT dataset on an Ottawa 20/30 sand sample, which provided an excellent porous frame for future computational studies. In the same report, we described a sequence of image processing approaches for generating a range of different hydrate cementation styles for elastic property calculation, spanning classical contact, coating, and pore-filling models described by contact cement theory (CCT).

We have pushed forward calculation of elastic properties using these models. We have developed a MATLAB interface to allow effective utilization of Garboczi's ELAS3D 3D finite-element code in an automated context. The interface performs automatic recompilation of the original F77 code to allow variations in problem size and property as well as automatic calculations on large model suites. The interface has been validated on example problems included in the original code documentation (e.g. spherical inclusions) and tested for scaling out to problems on the order of 250^3 voxels (15×10^6 unknowns).

In the last quarter, we continued our effort to generate estimates of elastic properties as a function of hydrate saturation for a range of different cementation styles as discussed in prior reports. In Q3, we completed a sequence of scripts which enable automated calculation of bulk and shear modulus for sub-volumes of a larger 3D image sequence. We initiated tests of this codeset that is now running on the pore realizations developed earlier in the project. The first set of runs considered a small set of 90^3 and 100^3 sub-volumes of the 389^3 full volumes from the "coating" scenario sequence. Hydrate elastic properties of 5.6 GPa (bulk modulus) and 2.4 GPa (shear modulus) were used with quartz and water properties applied for the grain and pore phases respectively. To achieve convergence, a large number of iterations (~10,000 conjugate gradient steps) were required for these geometries (2 hr wall-clock-time for 100^3 sub-volume); we are currently setting the code to run on a larger multicore machine to allow calculation for substantial sub-volumes and multiple realizations. Figure 1 shows porosity/modulus relationships for the calculated sub-volumes, color-coded for hydrate cement saturation. Dots with black lines are for 100^3 volumes while 90^3 volumes have no outer line. The relationships shown appear to be consistent (higher moduli associated with lower porosity); however, the smaller sub-volumes have increased scatter due to variable positioning with respect to grain boundaries.

In the next quarter, we aim to complete calculations for the different cementation scenarios and compare them to classical CCT models describing hydrate mechanical signatures. Utilization of larger sub-volumes (> 100^3 voxels) should enhance the stability of pore scale calculations.

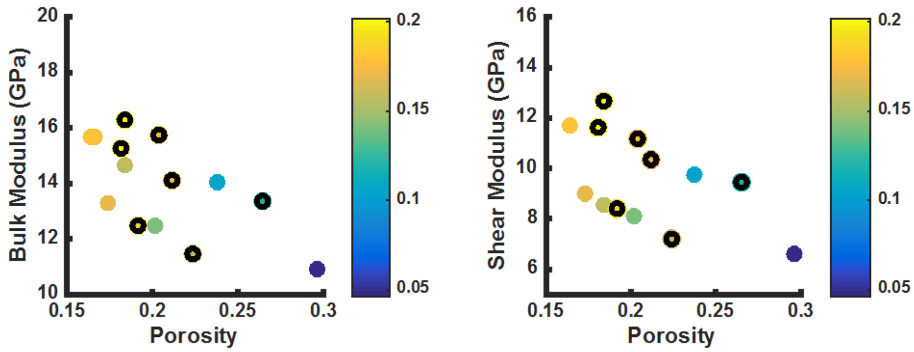


Figure 1 : Selection of sub-volume bulk (left) and shear (right) modulus calculations examining correlations between porosity and elastic properties during deposition of coating hydrates. The base image was a microCT volume acquired for an Ottawa sand sample. Hydrate saturations correspond to the color bar on the right of each plot. Here, porosity refers to remaining porosity (considers hydrate as part of the "mineral" space).

Task 8.0 Gas production from layered hydrate

The goal of this test is to examine the effects of small-scale anisotropy on hydrate formation and dissociation. In this test, we packed fine sand between thin layers of sandstone to simulate natural layering. Our experimental concept is shown in Figure 2a. We used Berea Sister Sandstone (Figure 2b. ~ 45 mD, 21.4% porosity) to represent our fine layers, and US Silica F110 sand for our coarse layers (~1 Darcy, 36% porosity). To model horizontally extensive layers thermally, we used PVC insulating material on the vertical sample boundaries (thermal conductivity 0.19 W/m.K) to simulate no heat flow, and aluminum spacers (thermal conductivity 205 W/m.K) on the top and bottom (Figure 2c) to encourage heat flow there. Heat flux sensors were used on three surfaces to attempt to understand the heat fluxes in a layered system.

We had some difficulties in our setup. The most difficult part was sealing the 12 wires (Figure 2d) extending from the heat flux sensors (HFS). Each HFS is composed of a thermopile (a number of thermocouples connected in series) and a local thermocouple resulting in 4 insulated wires from each. Pressurized gas will flow between the metal wire and plastic (Teflon in this case – difficult to epoxy) insulation. We have had success in the past stripping the wires in small bands at different lengths so the stripped wire locations don't cross, and potting the parallel wires in a stainless steel tube. To pass the 12 wires through the end cap, we used compression seal fittings. Off-the shelf modules are available that contain both thermocouple wire and conductors. Because they are off-the-shelf, internal connections (HFS to conductor) are needed. We used pin connectors for the thermocouple wires, and lacquered the final connection with an electrically resistive lacquer and adhesive-filled heat-shrink tubing in hopes of maintaining electrical isolation. This required adding two high-pressure couplings to accommodate the wiring.

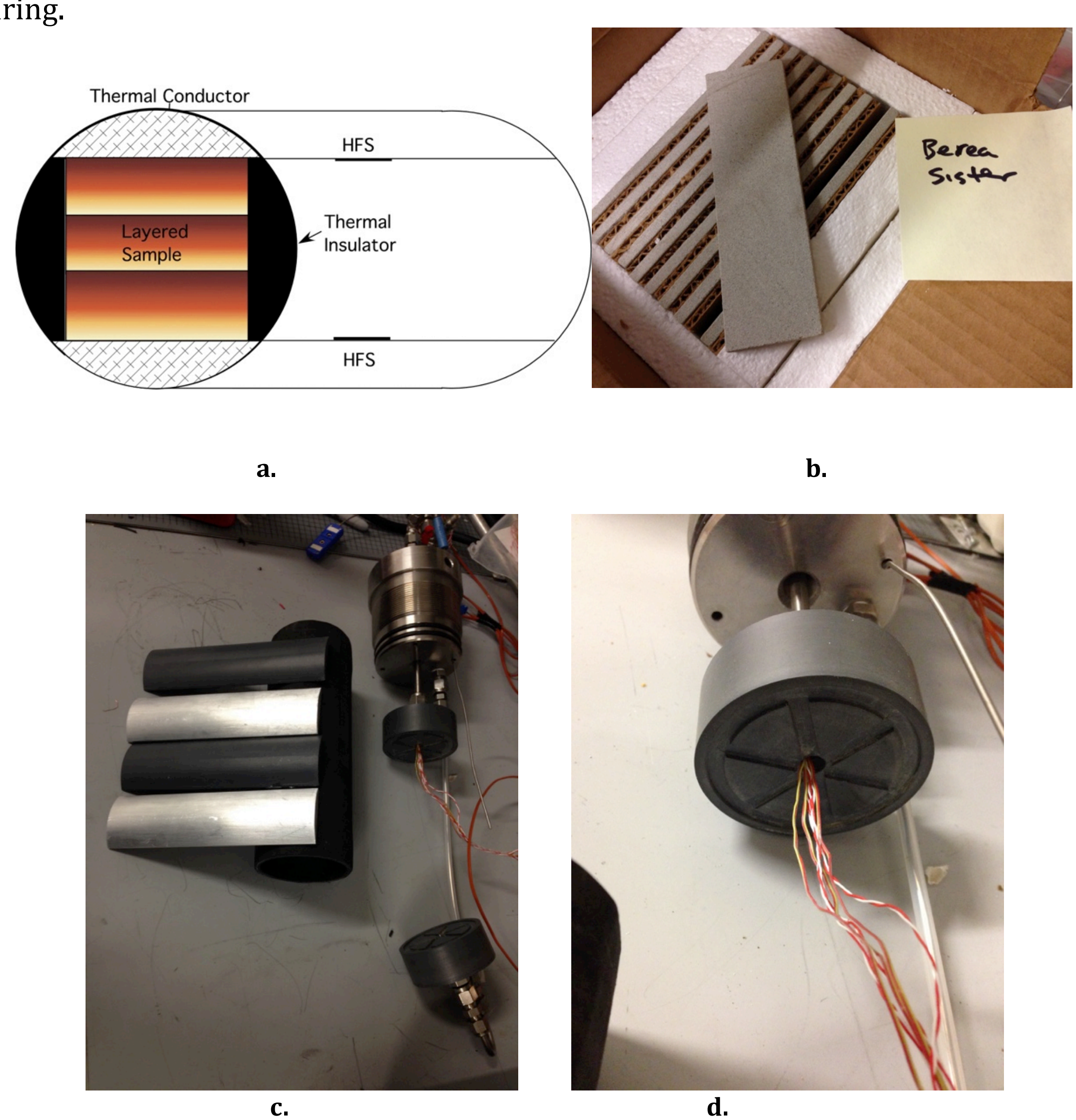
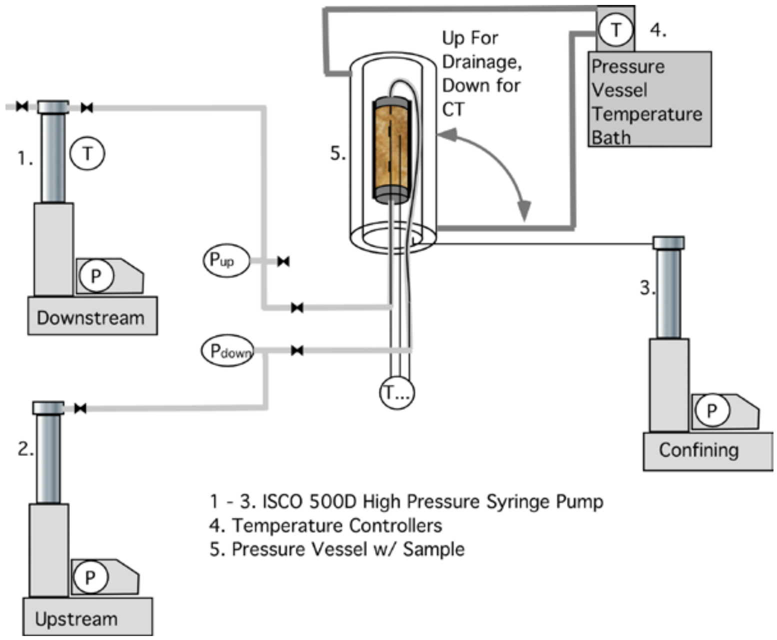
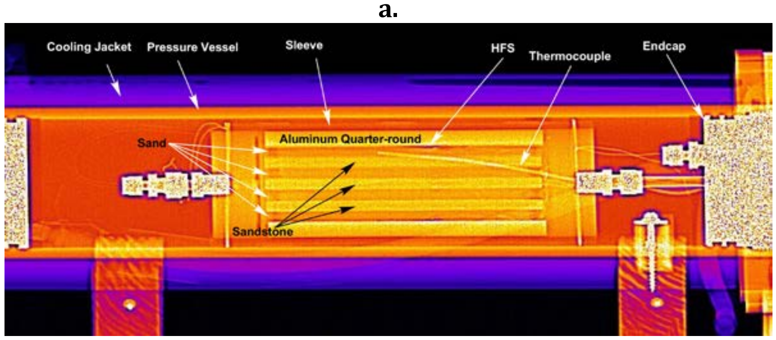


Figure 2. a. Layered sample geometry, b. Berea Sister rock slabs, c. vessel internals including aluminum and PVC spacers, and d. heat flux sensors (HFS) wires and endcap.

Test assembly was challenging (Figure 3) and required five repeats of system packing and assembly to address proper sand packing, spacer layout, leak elimination, and sleeve seal. Because of the thin wires and rough conditions of the rock and sand, in the process, we lost partial functionality of two of the three of our HFS devices after startup.



a.



b.

Figure 3. a. system schematic, b. sample and pressure vessel assembly.

Hydrate formation was documented by frequently collected pressure, temperature, and volume data (Figure 4), and intermittently by X-ray CT (Figure 5). Fifteen sets of CT scans were taken using both 80kV and 120 kV energies (288 slices/energy/scan) in hopes of using the differences between the energies to infer processes. These results require substantial processing and have shown little promise, likely because there are relatively constant differences in attenuation between 80 and 120kV for the elements in the test. Changes in higher atomic number elements are more readily identified using this technique.

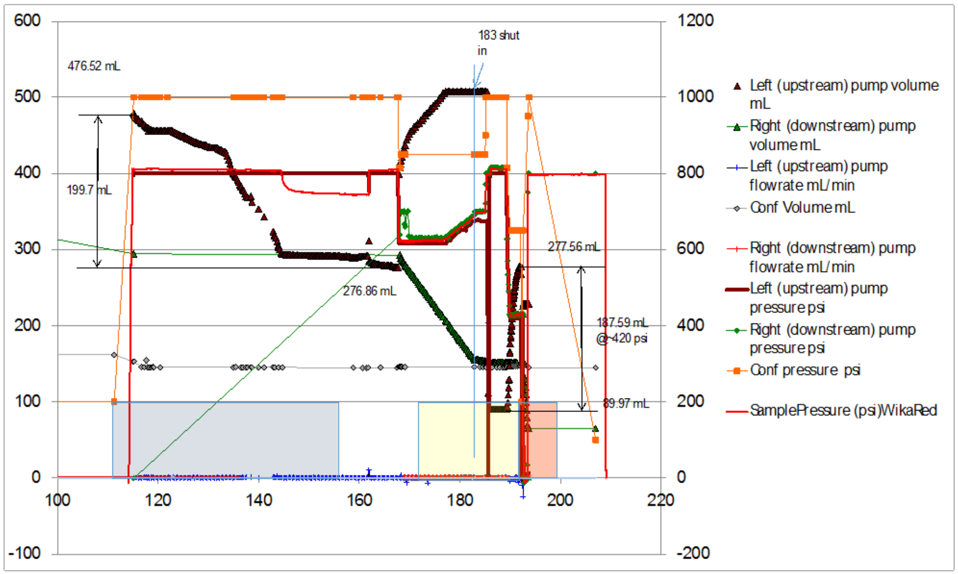


Figure 4. Pressure, temperature, and volume measurements during the hydrate formation (blue box), resaturation (yellow box) and dissociation (orange box) stages.

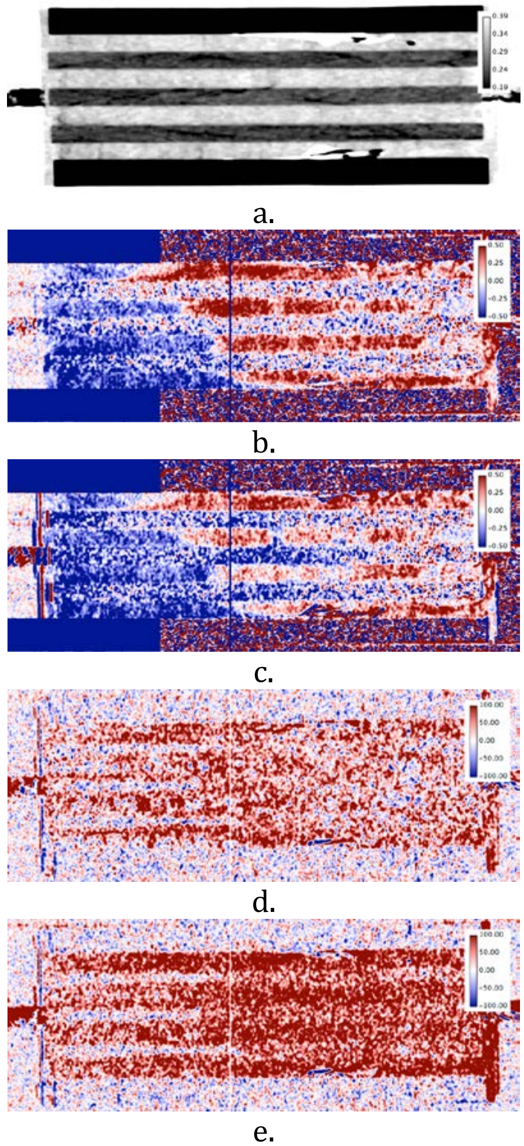


Figure 5. Central vertical axial cross-section showing a. porosity (fraction), b. density change upon hydrate formation (g/cm^3 step 3 of 6), c. density change upon hydration formation (g/cm^3 step 6 of 6), X-ray attenuation change during dissociation (Hounsfield Units (HU)~ 0.001 g/cm^3 step 2 of 8), and X-ray attenuation change during dissociation (HU step 8 of 8.). The center odd vertical slice of b.-e. is an internal standard placed in the image processing. In b. and c. the red shows increasing density from hydrate formation and water migration predominantly in the larger porosity regions (note sandstone is lower porosity and there is little change there). In d. and e. red indicates density decrease from gas formation during dissociation.

In the next quarter, we will complete analysis and share this data set (nearly 22 Gb of data) for interpretation by others. The influence of layers of varying parameters will be investigated. Currently four porosity regions are considered (Figure 5. - 0.18-0.23, 0.24 – 0.29, 0.30-0.36, and 0.36 – 0.39). These are the "valley-to-peak" ranges of the porosity histogram.

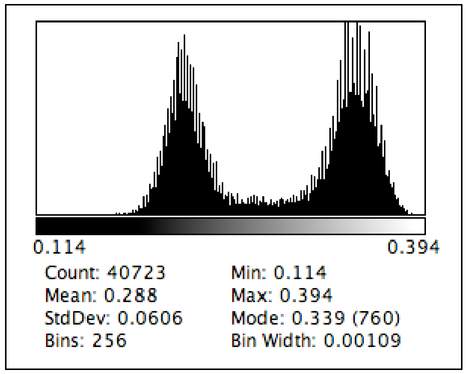


Figure 5. Porosity histogram. Note value ranges 0.18-0.23, 0.24 – 0.29, 0.30-0.36, and 0.36 – 0.39 correspond to the four valley-to-peak ranges.

Task 9.0 Comparison of dissociation in hot and cold hydrate

Not currently funded - No progress

Task 10. Vessel design and Modification

The LBNL X-ray transparent pressure vessel system will be redesigned and rebuilt to allow investigation of thermal and salinity gradients. Multiple entry and exit ports will be required for each phase on each end to allow simultaneous addition and withdrawal of fluid at each end of the sample to maintain a desired concentration gradient with as many as four ports required on each side for gradient control of both phases. Additional monitoring and temperature control devices will be added as well, including electrical conductivity probes.

The first step in the redesign will only be detailed enough to allow engineering review and preliminary approval. A go-no go decision will be made at the end of this step before continuing with Task 11.

Title: Engineering feedback on preliminary redesign
Planned Date: September 30, 2015
Revised Date: June 15, 2016
Verification Method: Revisions to schematic drawings

Progress: To date, we have provided a verbal description of our upgrade to the LBNL Engineering Pressure Safety Engineer while showing our current capabilities. Because we intend to use a simple tubular vessel with the complicated parts of the design incorporated into the massive endcap which is easier to produce under the necessary safety requirements, his perspective was the engineering would not be extensive, could be done by a vendor under LBNL review, and manufactured and tested off site. We have contacted two vendors and described our vessel. Both have extensive pressure experience, have worked on DOE projects in the past and will be able to do the work. Detailed designs for the purpose of cost estimation are in progress.

Our schedule has slipped on this task. This is advantageous as the design can allow incorporation of tests planned to investigate gas production from Ulleung Basin hydrates in a collaboration between DOE and KIGAM, and expanded tests to be included in NETL work. In the next quarter, we aim to complete the design, select a manufacturer, and proceed with vessel construction.

Title: New vessel construction complete
Planned Date: January 31, 2016
Revised Date: July 31, 2016
Verification Method: Photo of new vessel in lab

Task 11. Assessment of thermal gradient modification methods and Investigation of the effect of thermal gradient and gradient oscillation on hydrate behavior

Title: Test at least 2 gradient modification methods
Planned Date: December 31, 2015
Revised Date: February 26, 2016
Verification Method: Laboratory data showing results of tests

Progress: Multiple tests have been performed to examine the effect of thermal gradient. The results have been difficult to interpret as hydrate formation was inconsistent with the temperature gradient, and our control of the thermal gradient has not been as strong as originally hoped. The results from using temperature adjusting coils inside the pressure vessel (Figure 6.) indicated that the thermal influence of the coils was lower than expected.

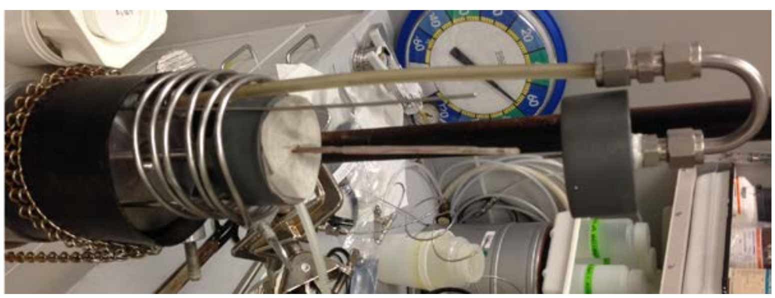


Figure 6. Temperature adjustment coils (left) located around the base of the sample inside the pressure vessel.

Title: Completion of successful test applying a thermal gradient, and oscillation of the gradient.
Planned Date: March 31, 2016
Revised Date: April 29, 2016
Verification Method: Production of complete data set for one test with temperature, pressure, X-ray CT data.

We are behind schedule on this because we have not been able to strongly control the temperature gradient. In the next quarter, we will consider baffle techniques to control confining fluid mobility and cooling jacket modifications for application of different cooling regions.

Task 12. Investigation of the hydrate dissociation point in saline systems with respect to gas production rate.

Title: Perform laboratory tests using analog ice/brine systems to provide information for hydrate/brine tests

Planned Date: March 31, 2016

Revised Date: June 3, 2016

Verification Method: Production of data set for one series of tests with temperature and rate information.

We have performed a number of tests forming methane hydrate in brine systems. Tests with brine will be completed on schedule. In the next quarter, we will complete analog tests and analyze the data generated to extend the results to the hydrate-brine system.

Project Spending*

Nov	Dec	Jan	Feb	Mar	Apr	May	Current FY Expenses	Budget Remaining
10,949	9,132	22,921	2,940	10,107	17,871	14,820	88,739	66,066

Table 1. Project spending in FY 2016 and remaining budget. Amounts from LBNL accounting information system on June 10, 2016 and provide the best estimate of expenses and budget as of that date.

National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

13131 Dairy Ashford Road, Suite 225
Sugar Land, TX 77478

1450 Queen Avenue SW
Albany, OR 97321-2198

Arctic Energy Office
420 L Street, Suite 305
Anchorage, AK 99501

Visit the NETL website at:
www.netl.doe.gov

Customer Service Line:
1-800-553-7681