Annual Report, Fiscal Year 2009
ESD05-048
Gas Hydrates Laboratory Research
Lawrence Berkeley National Laboratory

Introduction

Lawrence Berkeley National Laboratory has been performing laboratory research on the behavior of gas hydrate (particularly methane hydrate) in porous media for several years. Our program goals include providing information to facilitate the development of valid conceptual models of the behavior of gas hydrate in porous media, make measurements to aid in the simulation of hydrate-related processes in porous media, and to support the United States Department of Energy in its investigation of gas hydrate. LBNL has focused primarily on issues relating to producing natural gas produced from hydrate.

This report provides a summary of our progress on the tasks from our Fiscal Year 2009 work plan, which include performing a gas production test from a sample of hydrate-bearing core from the Mount Elbert Stratigraphic Test Well, estimating hydrologic parameters for the Mount Elbert samples, continued measurements and refinement of our capillary pressure measurement technique, measurement of geophysical and geomechanical properties of hydrate-bearing sediments, examination of different laboratory hydrate formation techniques, and the observation of changes in hydrate saturation over time under hydrate-stable conditions.

One of the most important questions pertaining to laboratory measurements on hydrate-bearing sediments (HBS) is whether the laboratory sample is uniform and representative. Uniformity is important because extensive (size-dependent, such as mass) measurements are made to infer intensive (size-independent, such as density) properties. To do this either requires the assumption of uniformity, or the ability to account for sample heterogeneity. Direct examination of HBS samples prior to performing a test is difficult. X-ray computed tomography (CT) scanning, used on many tests at LBNL is a technique that can be used to examine sample uniformity before, during, and after tests. How well a sample represents natural HBS sample is also critically important. For certain tests, the use of tetrahydrofuran hydrate may be appropriate to provide a representative sample, but for other tests may be inappropriate. Methane hydrate formed from excess gas typically cements sediment grains together, whereas indications from several deposits of natural HBS are that the hydrate is pore-filling or load bearing. Laboratory synthesis of uniform pore-filling hydrate samples has not been achieved or documented, although a variety of methods have been attempted.

Task 1: Gas Production Test on Preserved Mt Elbert Hydrate-Bearing Core

The objective of this task is to quantify the gas produced and observe processes occurring during the depressurization of a natural gas hydrate-bearing sample from Mt. Elbert. Figure 1 shows a schematic of the experiment setup. Two distinct regions are clearly visible in the sample (labeled A and B).

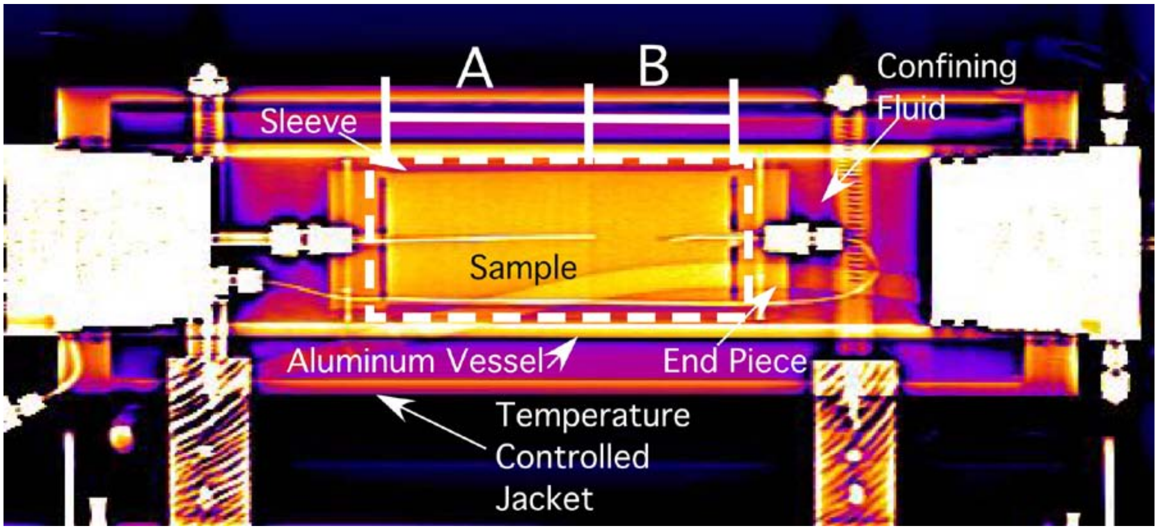

Figure 1. Sample is contained in a flexible sleeve between two end pieces. This assembly was placed into an x-ray transparent pressure vessel inside a temperature-controlled jacket.

Figure 2 (left) shows the initial density distribution at ten locations in the Mount Elbert sample, and the density changes over time (right) as the hydrate dissociates. As expected, hydrate dissociation occurs from the outside-in as heat for dissociation is supplied from the constant temperature bath.

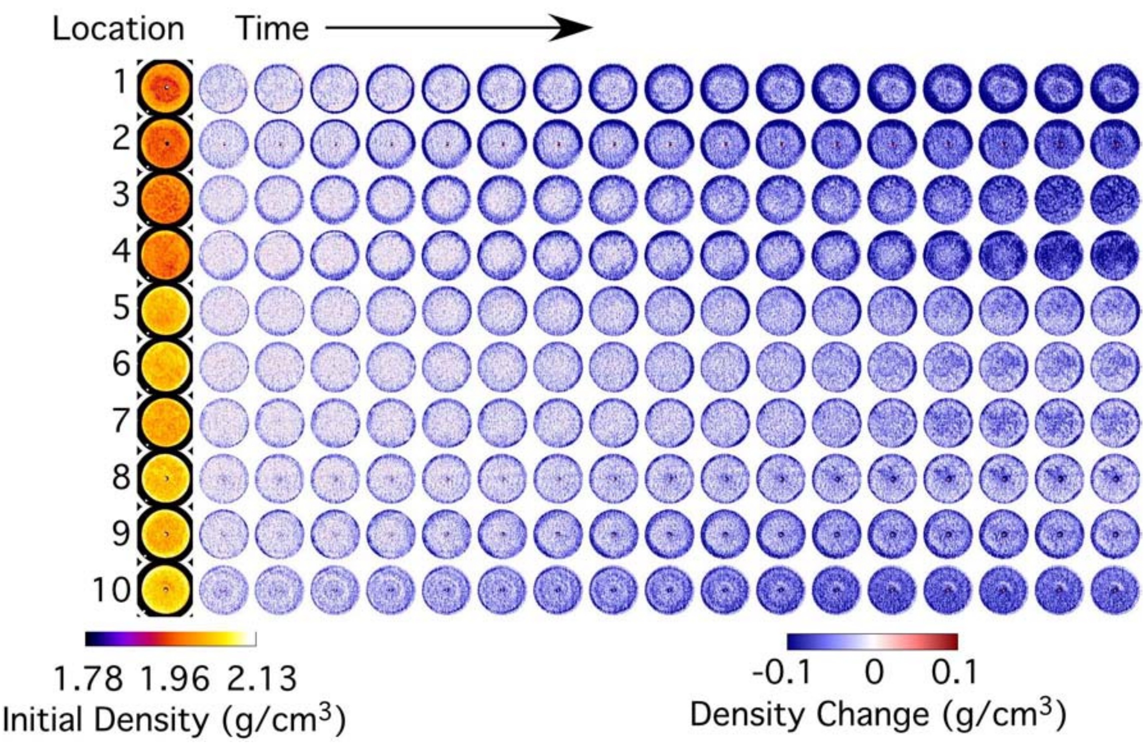

Figure 2. Initial density (left) and density changes resulting from dissociation by depressurization (right).

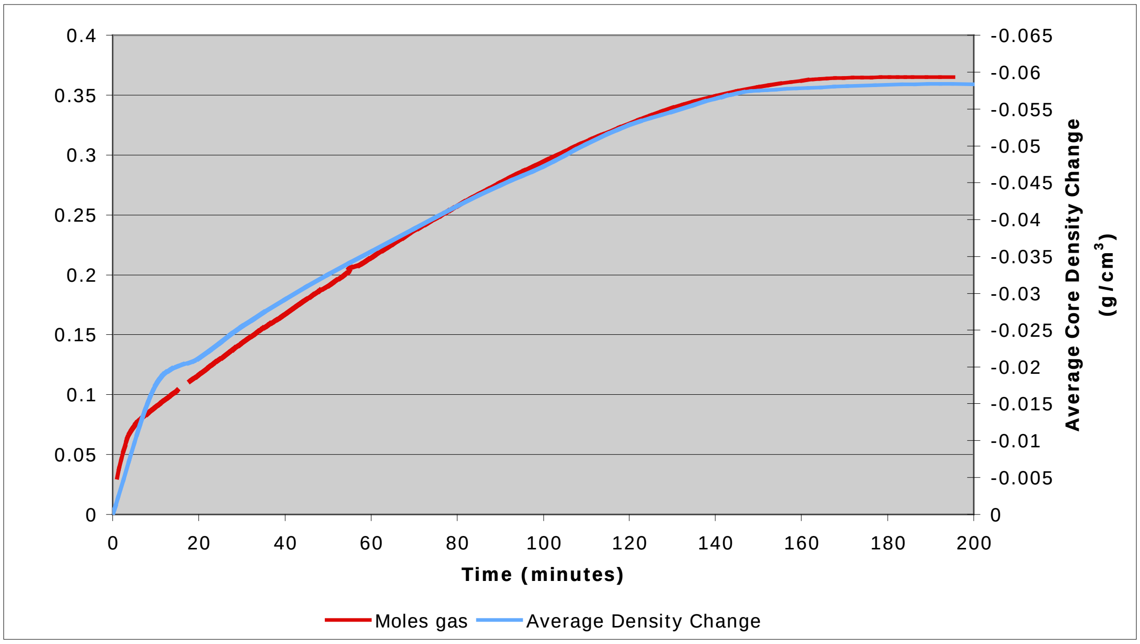

Figure 3. Moles of methane produced and the average core density change (by CT).

Figure 3 shows the moles of methane produced over the dissociation test, and the average core density change from CT data. The correspondence between the two data sets is quite good, although there is the potential that a small amount of water was coproduced as well. Analysis of the experiment data is ongoing for inclusion in a paper to be submitted to a journal.

Task 2: Estimation of Hydrologic Parameters for the Relative Permeability-Saturation and Capillary Pressure-Saturation Functions for the Mt. Elbert Core Samples using Inverse Modeling.

The objective of this task is to provide measurement-based estimates of the relative permeability and capillary pressure curves for Mt Elbert cores to aid in modeling. The recovered Mount Elbert cores showed a range of disturbance features (Figure 4), making ideal quantifications of the desired parameters difficult.

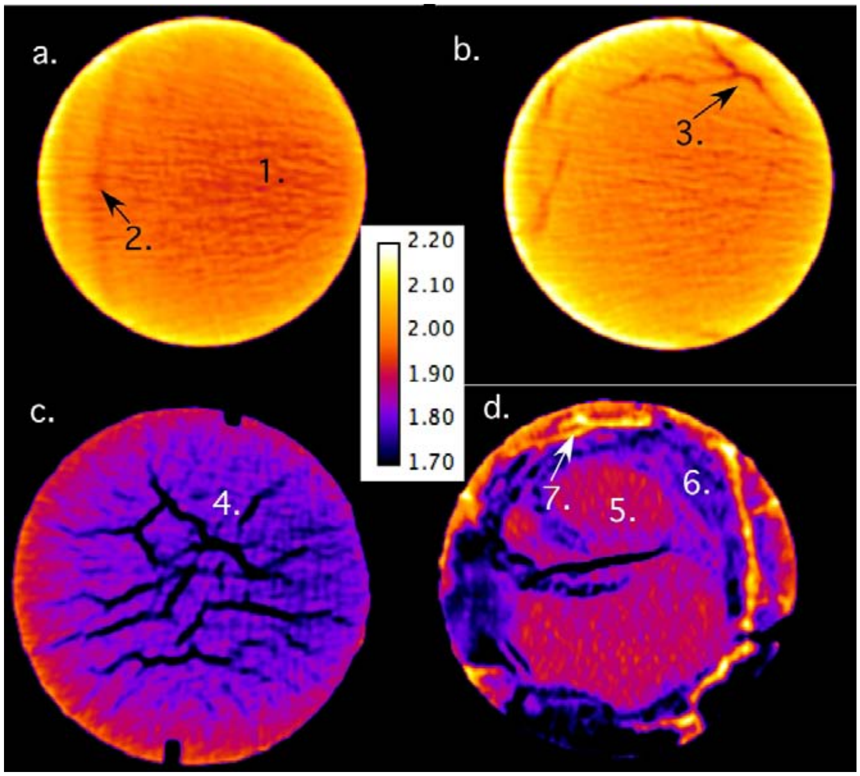

Figure 4. Examples of core disturbance observed in Mount Elbert Stratigraphic Test Well cores. (1 and 2 – CT artifacts, 3 – spalling-type fracture, 4 – radial fractures, 5 – less damaged region, 6 – strongly altered outer region, 7 – possible invasion of dense drilling mud). Reproduced from Kneafsey et al., 2009.

In spite of core damage, the core dissociated in Task 1 appeared relatively undisturbed, however it had been initially preserved by repressurization prior to chilling in LN. Because of this, secondary hydrate would be expected in the sample (Kneafsey et al., 2009). During the dissociation test, differential pressure data was collected. Because the test was performed by depressurizing the sample at one end, the differential pressure data with the CT data and subsequent permeability measurements were used to estimate effective and relative permeability values during the dissociation.

Capillary pressure tests have not been performed on the Mount Elbert samples. These will be performed with reformed subsamples that have recently become available following the completion of another set of tests (Task 6).

Task 3: Completion of the Combined Relative Permeability and Capillary Pressure Estimation Techniques using Laboratory Measurements and Inverse Modeling

The objective of this task is to develop a faster and more reliable technique to measure capillary pressure, and simultaneously obtain relative permeability information. The measurement of capillary pressure and relative permeability of hydrate-bearing sediments has proved to be experimentally and computationally challenging, with each experiment and numerical inversion requiring significant effort. Ultimately, to simulate gas production from specific hydrate-bearing reservoirs, reservoir-specific measurements using native samples will be needed. Quicker measurement techniques with less specialized equipment will be required for this purpose.

We performed a series of capillary pressure tests in FY09. In these tests, moist media was packed into a sample holder above a porous frit. Hydrate was formed by establishing the correct temperature and pressure conditions, and then the samples were carefully water flooded. The water was slowly withdrawn, and the difference in pressure between the water and gas phases (the capillary pressure) was monitored (Figure 5). These data are currently being processed and evaluated for inclusion in a paper to be submitted to the Society of Petroleum Engineers Offshore Technology Conference to be held in May 2010.

Figure 5. Example of capillary pressure data. Equilibrium measurements identified by lines and values in each graph are used in the capillary pressure determination. Transient data preceding the equilibrium are used for permeability calculations.

Task 4: Continued Laboratory Studies of Geomechanical Behavior of Oceanic HBS and Geophysical Signature of HBS Undergoing Thermomechanical Changes

The objective of this task is to continue measurements of the geomechanical behavior of oceanic HBS and the geophysical signature of HBS undergoing thermomechanical changes. Development and modification of two primary systems were required to perform this work; a modified split-Hopkinson-bar test (resonance) apparatus applied in either a steel or x-ray transparent aluminum/carbon fiber pressure vessel, and an x-ray transparent, acoustically-equipped (compressional and shear wave) triaxial test cell. The steel resonance apparatus was completed and tested, and primary calibrations have been performed. The first experiment in this cell using methane hydrate test was performed using a modified test procedure to test several hypotheses. These hypotheses include 1) the strength of the medium (as indicated by the resonance frequency) will increase with hydrate saturation, 2) spatial hydrate saturation distribution changes during hydrate dissociation will affect the measured resonance frequency and attenuation properties (typically dissociation initially affects the outer reaches of a sample – e.g. Figure 2), and 3) the habit of the hydrate can be changed (from cementing to pore filling – see Task 5) under certain conditions. The data obtained are providing guidance on refining the experiment approach such that data obtained are representative of the parameters needed.

The x-ray transparent triaxial cell (Figure 6) has been redesigned, remanufactured, and pressure-tested. Tests of geomechanical strength of HBS will begin in FY10.

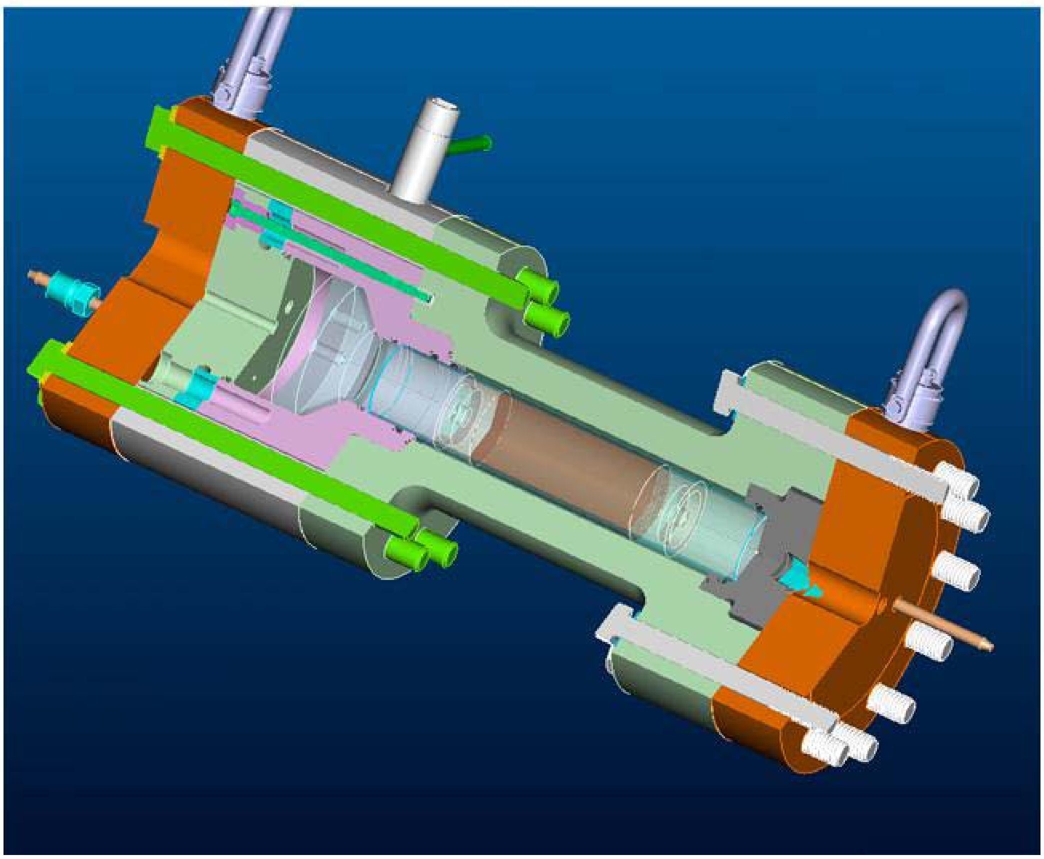

Figure 6. Cutaway drawing of the x-ray transparent geomechanical/geophysical test cell showing the sample (brown), end platens (adjacent to sample ends), and conical piston (transparent, left side) used to apply the axial load.

Task 5: Evaluation of Hydrate Formation Technique

The objective of this task is to evaluate and apply advances in hydrate formation techniques for uniformity and pore space occupation. Typical methane hydrate formation in the laboratory has focused on using pure water, methane, and silica sand, although a small number of tests have used natural sediments, and some have used surfactants. Uniform hydrate distribution is desired in lab samples because the models for which the measurements are made assume uniformity over the sample volume. Very few tests have demonstrated that a uniform hydrate (methane or any guest molecule) distribution has been achieved. Techniques have been suggested which may aid in uniform sample formation. These include the use of materials that aid in hydrate nucleation (e.g. colloids of biological cell membranes), and the presence of a small amount of salt.

The porespace occupation (pore filling or cementing) of the hydrate affects geomechanical, geophysical, and hydrologic properties. Recent research results indicate that the nature of the mineral grain cementation by methane hydrate is dramatically altered over many tens of hours following saturation of the pore space with water. This may indicate that the hydrate changes to a more pore-filling configuration.

We have performed a series of tests to examine the uniformity of hydrate formation, and the hydrate habit. For hydrate uniformity, the tests were performed using a fine sand at a moisture content we have typically formed quite heterogeneous hydrate saturation distributions. We have used pure water (baseline), water with sodium chloride, and water containing cell proteins normally used to induce ice crystal nucleation. We had hypothesized that the presence of sodium chloride (a hydrate inhibitor) would aid in more uniform formation because as the hydrate forms, the sodium chloride is excluded and becomes more concentrated in the liquid water phase, thus making continued formation more likely at other locations where the salt is less concentrated. Our results did not show this effect to be significant however, as a heterogeneous hydrate saturation distribution resulted. The hypothesis supporting the ice crystal nucleation enhancer was that if hydrate nucleation sites are present everywhere throughout the sample, hydrate formation should be able to start everywhere. The results of this test were unexpected. We expected hydrate to begin forming soon after conditions were correct, but hydrate formation did not begin for approximately 100 hours. Previous tests with long incubation times yielded very heterogeneous hydrate distributions, however in this test, the most uniform hydrate distribution for this sand/water combination was acheived.

Hydrate habit was inferred in a test in which hydrate was formed from excess gas in the modified split-Hopkinson bar apparatus. Upon hydrate formation, the sample stiffness increased dramatically over the moist sand. This increase in stiffness is attributed to hydrate cementing the sand grains together. The sample was allowed to age for several days with very little change in stiffness observed (slight increase in stiffness). The sample was then saturated with water. The sample stiffness decreased dramatically initially, and then slowly over the next several days. We interpreted this to be from hydrate reforming itself within the porespace into a pore-filling habit. Additional tests are needed to verify that this is indeed the cause, and not local hydrate dissolution at the water entry point or some other location.

Task 6: Observation of the Transient Behavior of Methane Hydrate in Porous Media Under Stable Conditions

The objective of this task is to observe and understand transient behavior of methane hydrate in porous media under hydrate-stable conditions. Methane hydrate was formed in the Mount Elbert core sample (Task 1) a number of times and allowed to age for up to six weeks. Intermittent CT scanning was performed along with constant pressure and temperature monitoring. Dissociation tests were performed on the sample, and then hydrate was allowed to form again after a period of time.

In this set of tests, we were able to track hydrate formation in samples from incubation through the establishment of stable conditions and then beyond. We expected to observe similarities between the repeated hydrate formations as the sample was the same and the bulk moisture content was approximately the same. During each formation, hydrate began forming in different locations and then grew outward from the nucleation point. Water was imbibed toward the forming hydrate as has been documented several times. Once the hydrate was stable (no further hydrate-related pressure or temperature changes) the periodic scanning was performed and continued changes in hydrate saturation were observed (Figure 7).

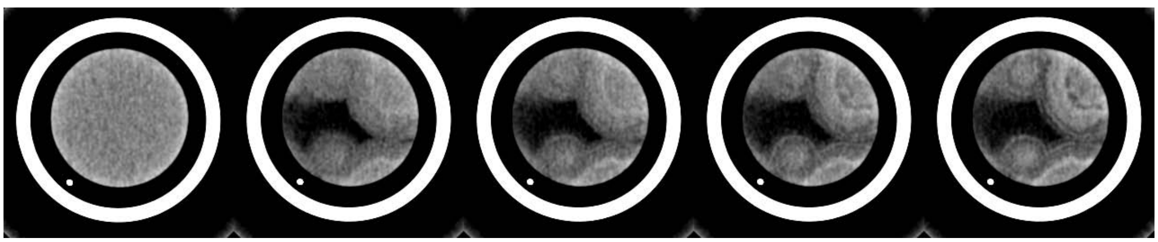

Figure 7. X-ray CT scans of a single location showing density changes over four weeks. The scan on the left is prior to hydrate formation. The hydrate reformed into rings of higher and lower saturation occurred under stable conditions.

This work was presented at the 2009 American Geophysical Union Fall Meeting, and a journal paper is in preparation describing the findings.

Papers and Presentations

Physical Properties of Hydrate-Bearing Sediments

Waite, W. F., J. C. Santamarina, D. Cortes, B. Dugan, D. N. Espinoza, J. Germaine, J. Jang, J. Jung, T.J Kneafsey, H. S. Shin, K. Soga, W. Winters, and T.-S. Yun (2009), *Physical properties of hydrate-bearing sediments*, Rev. Geophys., doi:10.1029/2008RG000279, in press.

“This article reviews the current understanding of phenomena involved in gas hydrate formation and the physical properties of hydrate-bearing sediments. Formation phenomena include pore-scale habit, methane solubility, spatial variability, and host sediment aggregate properties. Physical properties include thermal properties, permeability, electrical conductivity and permittivity, small-strain elastic P and S wave velocities, shear strength, and volume changes resulting from hydrate dissociation. The magnitudes and interdependencies of these properties are critically important for predicting and quantifying macroscale responses of hydrate-bearing sediments to changes in mechanical, thermal, or chemical boundary conditions. These predictions are vital for mitigating borehole, local, and regional slope stability hazards; optimizing recovery techniques for extracting methane from hydrate-bearing sediments or sequestering carbon dioxide in gas hydrate; and evaluating the role of gas hydrate in the global carbon cycle."

Mt. Elbert Core Disturbance Examination

Kneafsey, T.J., H. Lu, W. Winters, R. Boswell, R. Hunter, T.S. Collett, *Analysis of core samples from the BPXA-DOE-USGS Mount Elbert gas hydrate stratigraphic test well: Insights into core disturbance and handling*, Marine and Petroleum Geology (2009), doi: 10.1016/j.marpetgeo.2009.10.009

In this paper, disturbances to 11 core samples collected during the Mount Elbert Stratigraphic Test Well were examined. The samples were initially preserved two ways, 1) rapid cooling by immersion in liquid nitrogen (LN), and 2) repressurization with isotopically distinct methane and later depressurization and immersion in LN. The disturbances included radial fracturing, spalling-type fractures, loss of hydrate in the outer reaches of the sample, and secondary hydrate formation in initially pressure-preserved samples despite subfreezing temperatures. Laboratory tests were performed to gain insights into the disturbances. Radial fractures were attributed to the rapid freezing, spalling-type fractures may have been induced by rapid freezing as well, but mechanical disturbances during coring may also induce these fractures. Core subsampling and hydrate quantification showed the lack of hydrate in the outer regions of the LN-preserved sample, and isotopic analysis showed secondary hydrate formation throughout the pressure-preserved core with its effect being most prevalent in the outer regions.

Comparison of Hydrate Dissociation Observations and Simulations

Gupta, A., G.J. Moridis, T.J. Kneafsey, and E.D. Sloan, *Modeling Pure Methane Hydrate Dissociation Using a Numerical Simulator from a Novel Combination of X-ray Computed Tomography and Macroscopic Data*, doi:10.1021/ef9006565

In this paper, the dissociation of a porous methane hydrate sample was modeled using TOUGH+HYDRATE and compared to data collected and CT observations. This modeling was an extension of the TOUGH+HYDRATE concept to a sample that did not contain any mineral medium. A small fraction of the hydrate was assumed to be the supporting skeleton for the remainder of the hydrate. The modeling results compared favorably to the data.

Presentations

AAPG Annual Convention and Exhibition in Denver (6/7-6/10)

T. Kneafsey, W. Waite, H. Lu, G. J. Moridis, W. Winters, R. Hunter, M. Walker, *Hydrate-Bearing Sample Alteration from Core Retrieval, Handling, and Preservation*

This poster presented preliminary findings on Mount Elbert Stratigraphic Test Well core disturbance resulting from core collection, handling, and preservation. This work was later expanded and published in the Journal of Marine and Petroleum Geology.

Y. Seol, and T. J. Kneafsey, *Relative Permeability Parameter Estimation for Laboratory-Formed Hydrate-Bearing Sediments,*

This poster presented results of numerical simulations to extend laboratory permeability measurements.

National Research Council

Kneafsey, T.J., *Hydrologic, Geomechanical, and Geophysical Measurements on Laboratory-Formed Hydrate-Bearing Samples*

This invited presentation provided an overview of LBNL's gas hydrates laboratory program to the National Research Council Meeting of the Committee on the Assessment of DOE's Methane Hydrate Research and Development Program: Evaluating Methane Hydrates as a Future Energy Source on March 5, 2009.

Presentation and Collaboration Discussion at NETL

Kneafsey, T.J., *Water Migration During Hydrate Formation and Dissociation and Geomechanics of Hydrate-Bearing Sediments*, NETL, Morgantown. WV.

The presentation showed preliminary data examining water migration during hydrate formation. In addition, LBNL laboratory work on geomechanical strength of hydrate bearing sediment was presented.

AGU Fall Meeting, 2009, San Francisco, CA,14-18 December, 2009

T. J. Kneafsey, H. Lu, W. J. Winters, R. Boswell, R. B. Hunter, T.S. Collett, *Effects of core retrieval, handling, and preservation on hydrate-bearing samples*. OS31A-1191

This poster presented preliminary findings on Mount Elbert Stratigraphic Test Well core disturbance resulting from core collection, handling, and preservation. This work was later expanded and published in the Journal of Marine and Petroleum Geology.

Y. Seol, T. J. Kneafsey, E. V. Rees' *X-ray CT observations of methane hydrate distribution in natural sediment and laboratory formed compacted sand samples*. OS31A-1193

This poster presented observations of methane hydrate forming in unsaturated sand, and changes in hydrate saturation that occur under hydrate stable conditions. In addition, formation tests were repeated under similar and different conditions, resultine in different hydrate saturation patterns indicating that although the memory effect was occurring, other factors were also influencing hydrate formation.

*T. Kwon, G. Cho, J. Santamarina, H. Kim, J. Lee, *Stability evaluation of hydrate-bearing sediments during thermally-driven hydrate dissociation*. OS31A-1206

This poster presented the results of a modeling study examining the geomechanical effects of heating a hydrate-bearing strata (e.g. intentional thermal dissociation or accidental from pumping warm fluids such as oil through a well).

*E. V. Rees, C. Clayton, J. Priest, P. J. Schultheiss, *High volume methane gas hydrate deposits in fine grained sediments from the Krishna-Godavari Basin: Analysis from Micro CT scanning*. OS31A-1192

High resolution three-dimensional imaging of hydrate samples was used revealing high volumes of gas hydrate formed in vein structures in a fine grained clay. Analysis of the geometry of the veins showed a preference for the veins to grow in two distinct orientations. The volume analysis showed hydrate contents of between 8% and 60% in some core sections. These conclusions raise the following question: What impact would the dissociation of such a hydrate deposit have on host sediment properties, as clays are sensitive to fluctuating water content and salinity, and changes in both can affect sediment strength. High volumes of hydrate can occur in a grain displacing nature in a fine grained sediment, and if dissociated, could cause a large influx of fresh water, which would change the host sediment's water content and salinity. Analysis of these potential changes can be done by measuring host sediment properties.

*LBNL authors, however work performed primarily at other institutions.

Kneafsey, T.J. et al., 2009. Analysis of core samples from the BPXA-DOE-USGS Mount Elbert gas hydrate stratigraphic test well: Insights into core disturbance and handling. Marine and Petroleum Geology, In Press, Corrected Proof.