Oil & Natural Gas Technology

DOE Contract No.: DE-AC02-98CH10886

Final Report

Characterization and Decomposition Kinetic Studies of Methane Hydrate In Host Sediments Under Subsurface-mimic Conditions

Submitted by:
Energy Sciences & Technology Department
Brookhaven National Laboratory
Upton, NY 11973

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

August 2008

Office of Fossil Energy

Project Summary Page

Characterization and Decomposition Kinetic Studies of Methane Hydrate In Host Sediments Under Subsurface-mimic Conditions

DOE Contract No.:	DE-AC02-98CH10886
Contractor Names:	Brookhaven National Laboratory, Upton, NY
DOE Award:	$ 50,000
Principal Investigator:	Devinder Mahajan
Project Manager:	Traci D. Rodosta - National Energy Technology Laboratory
Type of Report:	Technical Report
Reporting Period:	May 2007 to May 2008

DISCLAIMER

SUMMARY

The purpose of this ongoing study is to establish sediment lithology and quantification of methane in hydrates hosted in sediments from marine sites of methane hydrate occurrence. For the reporting period of May 2007 to May 2008, our focus was on the quantification of macro- and micro-level changes in lithology that accompany decomposition of methane hydrates hosted in fine-grained sediments. To accomplish this goal, the BNL seafloor-mimic unit namely, Flexible Integrated Study of Hydrates (FISH), was first modified to allow formation of both unconsolidated and consolidated samples, at the macro level, of methane hydrates hosted in depleted fine sediments, recovered from the Gulf of Mexico (GoM). The macro level study was complemented by a study at the micro level for which the X-ray Computed Microtomography (CMT) technique at the Bemline X-2B, National Synchrotron Light Source (NSLS), BNL was utilized. Results for the CMT study of the tetrahydrofuran (THF)/water/glass beads, a reference and surrogate system for methane hydrates in sediments, are reported here. The highlights of the work are summarized below.

FISH unit modifications

The original FISH unit was configured for formation of methane hydrates in sediments as unconsolidated cores. The unit was modified to allow formation of cores under confined conditions that represent methane hydrates below the seafloor. Under Task 1, the key changes were as follows:

- Addition of a customized Temco DCHR core holder (D-1357-4).
- Addition of precision flow meters.
- Addition of overburden pressure Isco pump.
- Sediment and water control within the cells
- Temperature, Pressure and Gas delivery measurements and Cell cooling capability.
- Addition of Labview for data collection

In the modified FISH unit configuration, both the Jerguson see-through and the Temco vessels can be operated, individually or simultaneously- the former producing unconsolidated and the latter consolidated methane hydrates cores.

FISH unit- Measuring hydrate formation/decomposition at the macro scale

The characterized sediments were used as hosts to form methane hydrates at the *macro level* (sample size: 50-400 g) in the FISH unit that mimics subsurface conditions. Of the two vessels in the FISH unit, the Jerguson vessel was used to form *consolidated* hydrates that are representative of hydrate mounds formed from gas seepage and naturally found on the seafloor. The second vessel, Temco, was used to from *consolidated cores* (2” diamter x 6” long) under an overburden pressure that is more representative of large deposits of natural hydrtaes found several hundred meters below the seafloor. The effect of overburden pressure on hydrate satruration was quantitatively measured in the FISH unit by following methane consumption/evolution under Task 2.

Unconsolidated cores. A total of 11 runs were completed under Task 2.1. The formation/dissociation of methane hydrates hosted in the BLR and the GoM sediments in

the original FISH set-up (Jerguson cell) was achieved at P: 900-1500 psi and T: 2 – 4 ^{o}C. The key observations from the collected data are as follows:

- The coarse BLR sediments formed larger masses of hydrate that excluded sediments, whereas the fine-grained GoM sediments typically formed tiny nodules/veins against the glass of the vessel, with the remaining gas uptake apparently arising from hydrates dispersed within the sediments.
- The dissociation kinetics with the GoM and the BLR sediments showed that:
    - the warmer the temperature of hydrate formation or dissociation, more the temperature drop while dissociation.
    - as the pressure drop for hydrate dissociation (Peqm-Psys) increased, the sediment required more time for temperature to warm up after dissociation.

Consolidated cores. **A** total of 8 runs were completed under Task 2.2. The consolidated cores were formed from the water/saturated Ottawa sand/methane reference system in the FISH unit fitted with the Temco cell and then the decomposition was monitored. The observations from the collected data are:

- Hydrate dissociation with the depressurization technique resulted in an instantaneous gas output as high as 50 L/min for both 100 and 200 psi pressure drops below the equilibrium pressure.
- The greater the pressure drop during dissociation, the higher the degree of cooling. A longer time period was observed for sediments to reach initial in-situ temperatures.
- The presence of methane hydrate in sediments was confirmed by post-depressurization PT equilibrium that slightly shifted towards higher pressure from the theoretical pure methane hydrate PT stability curve. The enthalpy of dissociation of methane hydrates was calculated to be 59.134 kJ/mol using the Clausius-Clapeyron equation.
- During an endothermic methane hydrate dissociation, the faster temperature drop was at the center (T3) and half-radius (T2) compared to that at the wall (T1) of the core. This observation confirmed that during dissociation both at 100 and 200 psi, the hydrate front started to dissociate from the center towards the wall.

CMT- Measuring hydrate growth at the micro scale

The sediment characterization, without and with hydrate, utilized X-ray Computed Microtomography (CMT) at the BNL-National synchrotron Light Source (NSLS) to study *samples at the micro level* (Sample size 0.1 – 10 g). Under Task 3, two subtasks were: 1) Data analysis tool develoepment and 2) Growth habit of THF-hydrate/glass beads system were completed.

Under subtask 3.1, a multi-step method was developed to construct reproducible 2-D and 3-D volume images after construction and rendering of the collected CMT data. The steps involved were: 1) Collection of 1200 views in an assembled file (.prj) in IPLab software, 2) Convert_x2b_netcdf_display.sav-routine for converting filename.prj to filename.volume, 3) Convert image sequence into raw data in ImageJ, 4) Raw data processing in Drishti, and 5) Volume rendering and applying transfer function in Drishti.

Under subtask 3.2, the THF-hydrate was formed at T: –3^{o}C and P: 1 atm from the THF/Water/Glass beads system. The presence of $BaCl_2$ for contrasting allowed operation at T< 0^{o}C without freezing. The observations from the collected CMT data are:

- The 2-D images and the grain-to-grain match between specific vertical cross-section images from different tomoscans taken with time indicated that the growth of hydrates displaced beads within the unconsolidated pack.
- The 3-D volumes rendered from stack of images from each tomoscan with time showed the growth of hydrate to be patchy and preferentially from already nucleated region.
- The data confirmed that the microstructural model of the hydrate-water-grain system as “pore filling, i.e. growing in pores” cementation model.

Work is now ongoing to first complete a set of data from with the GoM sediment samples in the FISH unit to form consolidated cores of methane hydrate. The CMT work is extended to image methane hydrate in depleted GoM sediments to observe methane hydrate growth behavior. Differences or similarities in the decomposition of hydrates from sediment samples with different characteristics and their associated growth habit may ultimately have a bearing on field assessments of hydrate occurrences and potential for uncontrolled methane release under perturbation and consequent impact on climate change.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. Background

Gas hydrates are located in permafrost and marine environments and show potential as a vast methane source worldwide. However, methane is about 17 times more potent greenhouse gas than CO_2 and the inherent instability of hydrate deposits to temperature and pressure changes leading to uncontrolled methane release poses severe constraints on methane production methods under consideration and more importantly, has consequences on climate change. It is now documented from the accumulated well log data that hydrates show a wide variation in gas saturation, nature of accumulation, and heterogeneity of host sediments even within a specific hydrate site (Collect, 1998). A suite of new techniques and tools (Murray et al., 2006) such as interval velocity method are being deployed to characterize and quantify gas hydrate concentrations in hydrate reservoirs (Dai et al., The Leading Edge, 2004). Marine hydrates constitute much larger deposits than those found in permafrost with accumulations that are several meters thick below the seafloor though hydrate mounds are also found on the seafloor, likely formed through gas seepage.

In nature, gas hydrates are found as deposits though in various forms such as layers and highly dispersed. The elastic properties against hydrate saturations for cores recovered from Mallik 2L-38 well from Northern Canada match one of the six physical models as hydrate supporting grain matrix. However, gas hydrate coring within the DSDP, ODP (*Booth et. al.,1998*) reveals that hydrates often exist as pure aggregation (massive bodies, nodules, layers) and disseminate as fracture fillings in the shallow shaly sediments. There is certainly a serious safety hazard involved during drilling operations, since hydrates can decompose into gas under wellbore conditions. When not avoidable, the hydrate stability zone is drilled and cased as fast as possible to minimize the risk of wall failure, perhaps leading to loss of the hole. The collapsed tubing in the USSR was attributed to hydrate dissociation *(Makogon; 1988*). Thus the microstructure of methane hydrate in host sediment impacts elastic properties of the host sediments and has implication on seafloor stability. A fundamental understanding of methane hydrate growth habits and decomposition behavior under mimic conditions will aid in understanding the potential role of this massive carbon reservoir in climate change.

II. Literature To date

Since field studies are expensive, the laboratory-mimic approach has been taken by many researchers to study these systems. Earlier studies focused on pure methane/water systems to form hydrates. But natural hydrates are invariably hosted in sediments that can influence both the nature of hydrate growth and other system properties. The hydrate formation/dissociation kinetic data can yield hydrate saturation as a function of depth data though there is paucity of kinetics data in natural sediments as hosts. The sediment size in natural hydrate samples varies from coarse to fine silt depending on the site. The grain-size classification is shown in Table 1.

Table 1: Grain-size classification based on the Udden-Wentworth scale (Wentworth, 1922)

Millimeters (mm)	**Micrometers (µm)**	**Phi (f)**	**Wentworth Size Class**	
4096		-12		
256		-8	Boulder	Gravel
64		-6	Cobble	
4		-2	Pebble	
2		-1	Granule	
1		0	Very coarse sand	Sand
0.5	500.00	1	Coarse sand	
0.25	250.00	2	Medium sand	
0.125	125.00	3	Fine sand	
0.0625	62.50	4	Very fine sand	
0.03125	31.25	5	Coarse silt	Silt
0.015625	15.63	6	Medium silt	
0.0078125	7.81	7	Fine silt	
0.00390625	3.91	8	Very fine silt	
0.00006	0.06	14	Clay	Mud

Recently, studies were reported by Winters et al (AAPG Hedberg Conference, 2004) and Kneafsey et al. (J. Pet. Sci. Eng., 2006) on hydrate formation in porous media, mostly with coarse sands as hosts. The present study is specific to methane hydrate-sediment interaction under marine-mimic environment in the laboratory.

III. Approach

At Brookhaven National Laboratory (BNL), our laboratory effort to study sediment-methane hydrate interaction consists of two tools:

- The sediment characterization, without and with hydrate, utilizes Computed Microtomography (CMT) at the BNL National synchrotron Light Source (NSLS) to study *samples at the micro level* (Sample size 0.1 - 10 g). The reconstrcution of CMT data yields 2-D and 3-D images from which: 1) porosity and 2) tortuosity values are extracted. The CMT data also allows visualization of hydrtae growth in porous media as a function of time. The observed hydrate struucture can be fitted into one of the six known hydrtae microstrucutre models.

- The characterized sediments are used as hosts to form methane hydrates at the *macro level* (sample size: 50-400 g) in the Flexible Integrated Study of Hydrates (FISH) unit that mimics subsurface conditions (Figure 1). Of the two vessels in the FISH unit:.

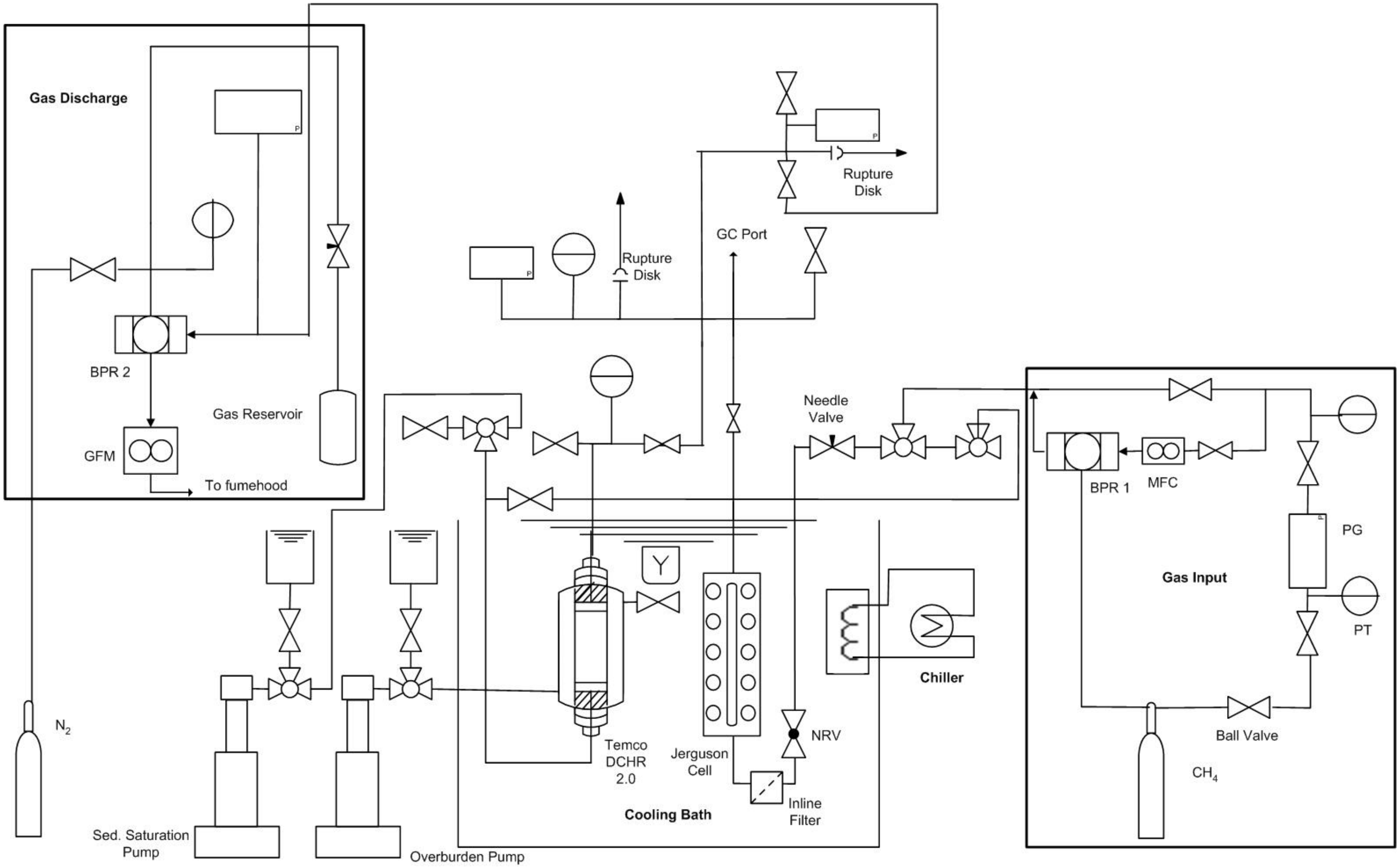


Figure 1. Process flow diagram for the FISH unit. Both Jeguson and Temco cells are shown.

- The Jerguson vessel is used to form *unconsolidated* hydrates that are representative of hydrate mounds formed from gas seepage and naturally found on the seafloor.

- The second vessel, Temco, is used to from *consolidated cores* (2”diamter x 6” long) under an overburden pressure that is more representative of large deposits of natural hydrates, several hundred meters below the seafloor. The varying overburden pressure can also affect hydrate satruration that is quantitatively measured in the FISH unit by following methane evolution during decomposition. The FISH unit data yields a temperature profile during depressurization to understand the methane hydrate dissociation behavior that is crucial to defining boundary conditions for its instability in the natural environment.

IV. Samples Used

For runs in the FISH unit, natural depleted sediments from two known marine hydrate sites in North America were used in this work. The Blake Ridge (BLR) sediment sample was from the ODP leg 164 (Latitude: 31° 48.210' N; Longitude: 75° 31.343' W; Hole/core: 995A-80X-1; Water Depth: 2278.5 m). Previous measurements of stress history and geotechnical properties of this core have been reported (Ginsburg, 1995) (water content: 39.3 % dry weight; porosity: 51.0 %; maximum past stress: 2730 kPa). The Gulf of Mexico (GoM) sediments used were from the JIP-Chevron cruise KC151, hole #3 (latitude 26° 49' 22.6" N, longitude 92° 59' 11.3" Wand 1 m sub-seafloor depth; Water depth at the drill location =1311 m). The GoM sediment sample was fractionated by sieving to screen sediment grains < 125 µm, the size defined as “fine-grained”. This sample was sent to Microtrac, Inc. for particle-size distribution analysis. The particle size distribution is shown in Figure 2. Note from Table 1 that the GoM samples fall in the “Very Fine Silt” to Clay category.

For the CMT study, two samples: 1) glass beads of uniform 500 µm size and 2) Ottawa sand, were used as reference.

IV.1. Characterization of host sediments

Sediment particle size may affect hydrate formation and dissociation kinetics. Two natural sediment samples from piston cores, GoM and BLR, were characterized with the scanning electron microscopy (SEM) technique. Figure 3a shows the SEM images of the GoM sediment sample. Figure 3 at 30KX magnification shows the majority of particle size to be < 2 µm. The values of 55% and 48.5% clay (< 2 µm) for samples from sites GC185 and MC852 respectively, were reported by Francisca et al. (2005). The BLR sediments are coarser and contain diatoms, accumulations of spicules and foraminifera. The Energy Dispersive X-ray (EDX) analysis of the same sediment samples shows the elemental composition (Figure 3b).

Figure 4a shows the SEM scan of a dried BLR sediment sample. Figure 4a taken at 1000X magnification confirms the diatom structure similar to that observed as part of foraminifera, diatoms, accumulations of spicules, sand-like microfossile debris, and pods and lenses of framboidal pyrite in the sediments from ODP Leg 164 (997A, 510 mbsf) by Lorenson (2000).

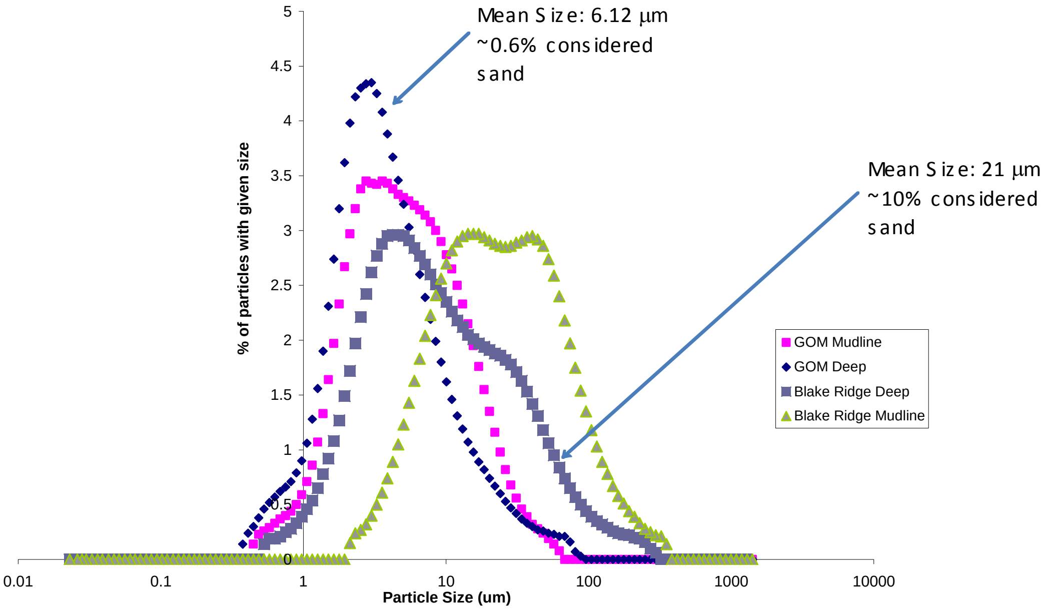
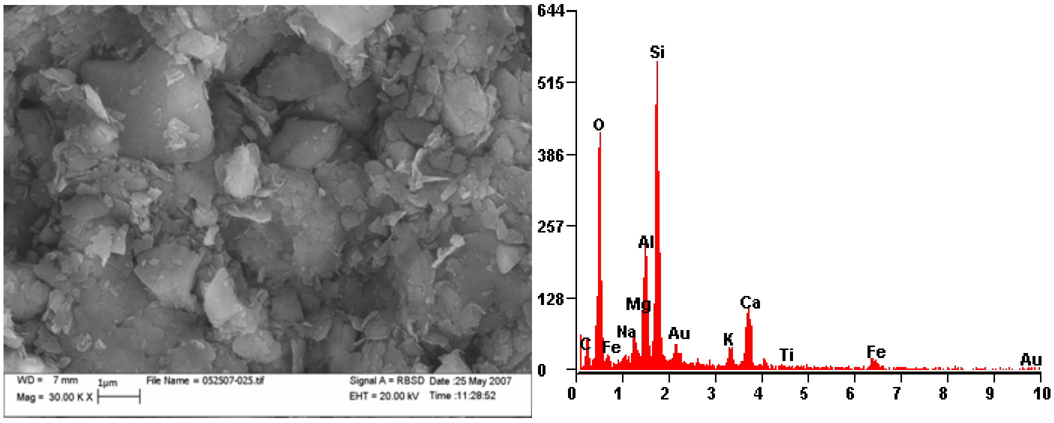
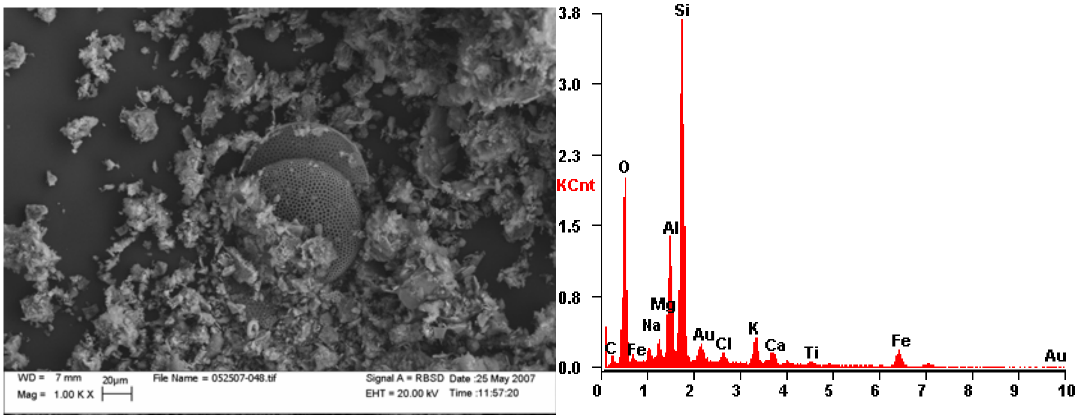


Figure 2. Particle size analysis of Gulf of Mexico (GoM) and Blake Ridge (BLR) sediment samples.



(a) **(b)**

Figure 3. (a) Magnified SEM image of GoM KC151-3 17H-4 sediment and (b) elemental composition from EDX analysis.



(a) (b)

Figure 4. (a) Magnified SEM image of BLR OC178 sediment and (b) elemental composition from EDX analysis.

V. Technical Work Description

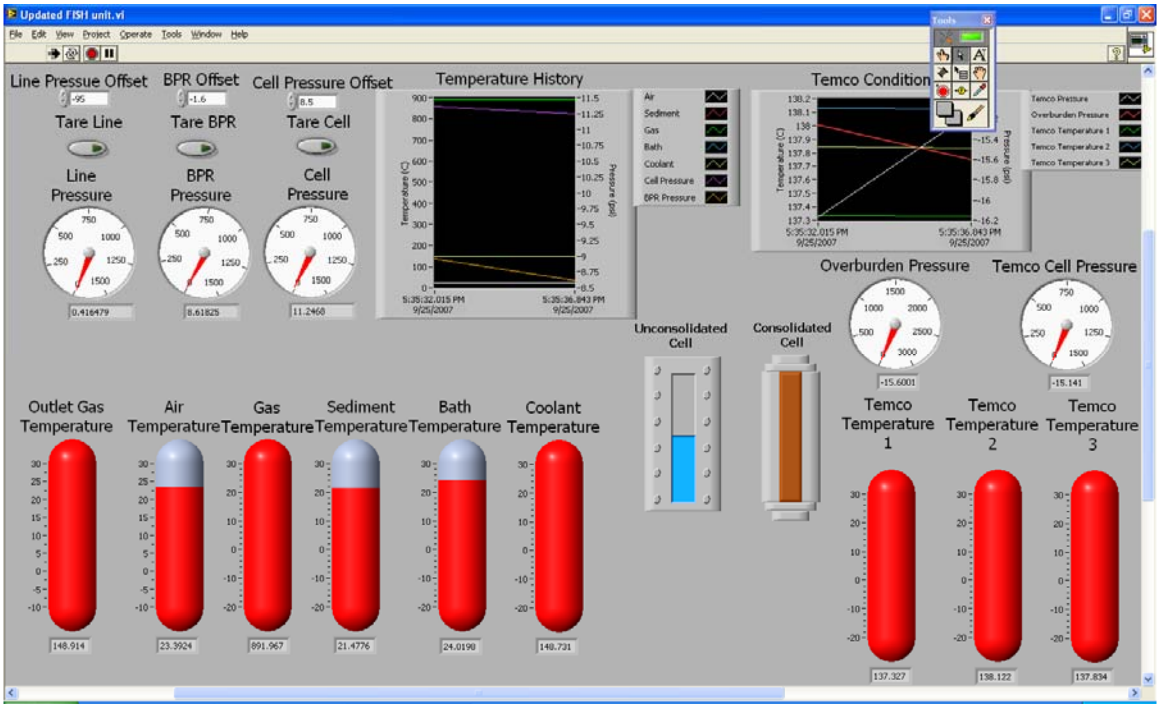
Task 1. Modification of the FISH unit.

The original FISH unit was configured for formation of methane hydrates in sediments without overburden pressure (unconsolidated). The unit was modified to allow formation of cores under confined conditions that represent methane hydrates below the seafloor. The key changes were as follows:

- Customized Temco DCHR core holder (D-1357-4). A high-pressure vessel (P_{max} = 34 MPa) capable of forming consolidated methane hydrate cores of maximum diameter 2" and length 6", held in a Viton 70 rubber sleeve was added to the FISH unit. The radial pressure applied by the fluid in the annulus gap around rubber sleeve simulates the reservoir overburden pressure.
- Methane hydrate saturation within a consolidated core with known water saturation can be determined from an accurate mass balance for methane gas metering during formation and dissociation. Both the input (during hydrate formation) and the output (during hydrate decomposition) of methane gas were measured by precision mass flow meters.
- Overburden Pressure Isco Pump- An Isco D Series Syringe Pump (100 DM), which can work in both constant-flow or constant-pressure (P_{max} = 67 MPa) modes, is used to apply overburden pressure on the core sample.
- Sediment and Water Control within Cell- A 0.5 µm stainless steel (SS) pore size in-line filter from Swagelok was placed on the top/bottom of the vessel to trap sediments in the confined volume. The SS poppet check valve installed below the fixed retainer of the Temco cell controlled the sediment within the vessel and prevented gravity-drainage of confined water.

- <u>Temperature, Pressure Measurement, Gas Delivery and Cell Cooling</u>- Three type J, 1/16" diameter and 24" long SS sheath with 116" long PFA coated lead wire (TJ84-ICSS-116U-24) were installed at different radial and lateral core (2" diameter and 6" length) locations. In addition, braided fiberglass insulated type J thermocouples were installed to measure air, refrigerated circulator bath, cell water bath and outlet water bath temperature. Gas delivery line pressure and cell pressure could be measured and displayed with strain gage pressure transducers (PX4100-1.5KGV) and display units (DP-25B-S-A) respectively. The overburden pressure of Temco cell was measured with pressure transducers of higher maximum pressure value (PX4100-3KGV).
- A National Instrument's (NI) Signal Conditioning Extension for Instrumentation (SCXI-1000) chassis houses, powers and controls the NI SCXI-1303 module, temperature, pressure and flow signals through the Labview software. A real time window of the data acquisition is shown in Figure 5.

In the modified FISH unit configuration, both the Jerguson see-through and the Temco vessels can be operated, individually or simultaneously, the former producing unconsolidated and the latter consolidated methane hydrates cores (Figure 1).



Line Pressue Offset -95
BPR Offset -1.6
Cell Pressure Offset 8.5
Line Pressure 0.416479
BPR Pressure 8.61825
Cell Pressure 11.2468
Overburden Pressure -15.6001
Temco Cell Pressure -15.141
Outlet Gas Temperature 148.914
Air Temperature 23.3924
Gas Temperature 891.967
Sediment Temperature 21.4776
Bath Temperature 24.0190
Coolant Temperature 148.731
Temco Temperature 1 137.327
Temco Temperature 2 138.122
Temco Temperature 3 137.834

Figure 5. A Labview real time data acquisition window layout.

Task 2. Sediment hosted methane hydrate formation/decomposition in the FISH unit.

Task 2.1. Unconsolidated cores

The Jerguson flat glass see-through vessel (Figure 1) was fitted in the FISH unit and used for this study.

Vessel features:

- Vessel volume: 198 mL
- Maximum working pressure: 20 MPa
- Windows: 12” long x 1” wide for visual monitoring
- Type of methane hydrate formed: Unconsolidated
- Forms methane hydrates in sediment samples from free water and methane gas.

Procedure

1. The pressure vessel is placed in the water tank of the FISH unit.
2. The vessel is filled up to about 30% with dry and weighed sediment.
3. Water (deionized (DI) or simulated seawater (SW)) is added from the top to the vessel containing sediment and the volume is measured.
4. The vessel is pressurized with CH_4 till the desired pressure is attained ($\leq$ 1500 psi). The pressurization involved reaching the desired system pressure by fast filling the vessel, i.e., at >2000 mL/min by bypassing the mass flow controller (static mode). As gas diffused into the sediment/water column and was hydrated, the overall pressure in the system decreased. To maintain a constant system pressure, metered gas was added to the system after a week to ensure a constant driving force for later formation. This method was more representative of the seafloor conditions where methane gas/water does not agitate the sediment and the methane hydrate formation phenomenon probably occurs mostly by diffusion. This system (including the vessel) pressure is maintained with a Back Pressure Regulator (BPR).
5. The vessel is cooled to 4^0C and maintained.
6. The pressure drop is monitored by a pressure transducer (error: ±1psi) that continuously records the drop in system pressure. The pressure drop is a quantitative measure of hydrate formation.
7. Periodically, CH_4 is charged to the system to maintain set pressure.
8. The process continues till no more CH_4 is consumed- this represents methane hydrate saturation in hosted sediment.

Data recording

1. The methane hydrate growth is also visually observed and recorded with a digital camera as a function of time.
2. The exact amount of consumed CH_4 is calculated from total drop in system pressure during a given run.
3. The Labview records T/P versus time data over the entire run.

Both the BLR and GoM sediments were used in the runs at T: 2^o-10^oC, P: 900-1500 psi, and Water: DI or SW. A summary of completed runs is shown in Table 2.

Table 2: Summary of runs completed with BLR and GoM sediments in the FISH unit fitted with the Jerguson cell.

Sediment	**Water**	**Formation Conditions**		**Dissociation Conditions**	**Note**
		P	**T**	**ΔP from Peqm**	
Amount, Type		**Psig**	**^{o}C**	**psi**	
57.8 gm BLR[a]	57.1 mL DI[c]	900	2	206 psi driving force	Formation kinetics and gas evolution rate
		1200	2	200 psi driving force	Formation kinetics and gas evolution rate
		1500	2	200 psi driving force	Formation kinetics and gas evolution rate
57.8 gm GoM[b]	57.1 mL DI[c]	900	2	78 psi driving force	Formation kinetics and P-T dynamics during dissociation
		1200	2	4 psi driving force	Formation kinetics and P-T dynamics during dissociation
		1500	2	143 psi driving force	Formation kinetics and P-T dynamics during dissociation
		1500	2.5	143 psi driving force	Formation kinetics and P-T dynamics during dissociation
		1200	6	---	
		1500	6	143 psi driving force	Formation kinetics and P-T dynamics during dissociation
		1500	10	Unknown driving force	Formation kinetics and P-T dynamics during dissociation
57.8 gm GoM[b]	57.1 mL SW[d]	1500	2	40 psi driving force	Formation kinetics and P-T dynamics during dissociation

[a] BLR = Blake Ridge sediment

[b] GoM = Gulf of Mexico sediment

[c] DI= Deionized water

[d] SW = Simulated seawater

The hydrates formed in BLR sediment were observed to be massive i.e. about the size of the entire sediment/water column. However, gas uptake and hydrate growth in the GoM sediments yielded very little hydrate outcropping (1-2 mm above the sediment column), indicative of very low gas holdup internally- most gas absorption was likely due to hydrate formation at the sediment/gas interface at the top of the column. Figure 6 shows the difference in behavior for both types of sediments. The more coarse-grained 667m BLR sediments appear to form "massive" exclusionary hydrates under 2°C and 1500 psi static conditions and leave behind a large void upon dissociation. The finer-grained GoM hydrates are much less distinct and dispersed and often times in "nodular" or "vein- like" structure.

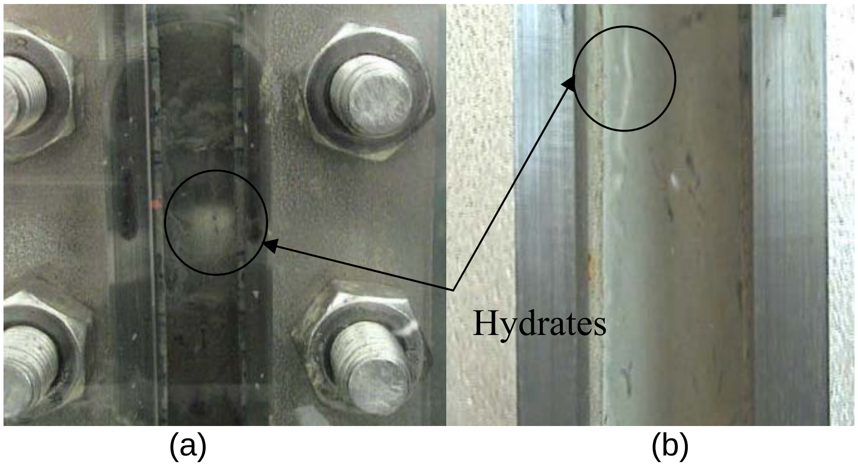


Figure 6. Methane hydrate formation at 2°C/1500 psi in (a) BLR and (b) GoM host sediments.

Figure 7 shows pressure drops for both the BLR and the GoM sediments at 1200 psi formation pressure. The figure also shows theoretically calculated values. The blue line represents the pressure drop in a mass-transfer limited system (i.e. the rate of reaction far exceeds the rate of diffusion) with kinetic rate constants. The non-porous GoM sediments very closely follow the theoretical trend (maximum deviation: 10psi). However, it begins to asymptote due to an apparent lack of continued formation. As gas travels through the sediment column, even at high velocities, the highly porous sediments fundamentally trap more gas as it percolates through the column, as well as the likelihood of a less-than optimal closest packing arrangement upon settling for larger (and naturally more porous) systems, such behavior may explain the faster uptake of gas in the BLR system as well as in 1200 micron glass beads. However, despite the increased amount of gas absorbed/hydrated, the curve still follows the asymptotic decay to the "no observable change" condition as in the GoM system. The hydrates formed in GoM sediments at 2°C and 6°C followed very similar trends but the initial growth rate was higher at 6°C than that at 2°C as predicted by the mass-transfer model.

The hydrate dissociation runs were performed on both sediments along with an additional run with GoM-simulated seawater system. In each case, the predicted fugacity difference was calculated based upon equilibrium predictions in pure water and pure methane.

Figure 8 shows the amount of cooling due to hydrate dissociation reaching to a zero-slope at the point of maximum temperature depression. The higher driving force results into rapid dissociation and hence faster endothermic effect. The higher temperatures for the same driving force yield faster dissociation kinetics and the accompanying faster temperature drop that results in faster cooling. Large particle sizes yield slower production of gas from hydrates, even at high driving forces due to a lower surface area, and will necessarily take longer to fully expend the hydrate mass. The hydrates formed in salt water appear, for similar conditions in pure water, to dissociate more rapidly.

The following observations are deduced from the data obtained:

- At a CH_4 flow rate of < 200 ml/min in to the vessel, a marked increase in gas uptake during hydrate formation was observed. This was true only with the BLR host sediments, likely due to an increased gas holdup in these coarse sediments.

- Methane hydrate formation rates in fine-grained sediments (mass transfer controlled) are in close agreement to theory, with the gas uptake spanning over 2 weeks. In larger, more porous sediments, gas uptake rate was significantly enhanced compared to that in fine-grained sediments.

- The coarse BLR sediments formed larger masses of hydrate that excluded sediments, whereas the fine-grained GoM sediments typically formed tiny nodules/veins against the glass of the vessel, with the remaining gas uptake apparently arising from hydrates dispersed within the sediments.

- The dissociation kinetics with the GoM and the BLR sediments showed that:
    - the warmer the temperature of hydrate formation or dissociation, more the temperature drop while dissociation.
    - as the pressure drop for hydrate dissociation (Peqm-Psys) increased, the sediment required more time for temperature to warm up after dissociation.
    - In comparison to the GoM sediments, the BLR sediments warmed up quickly after dissociation.

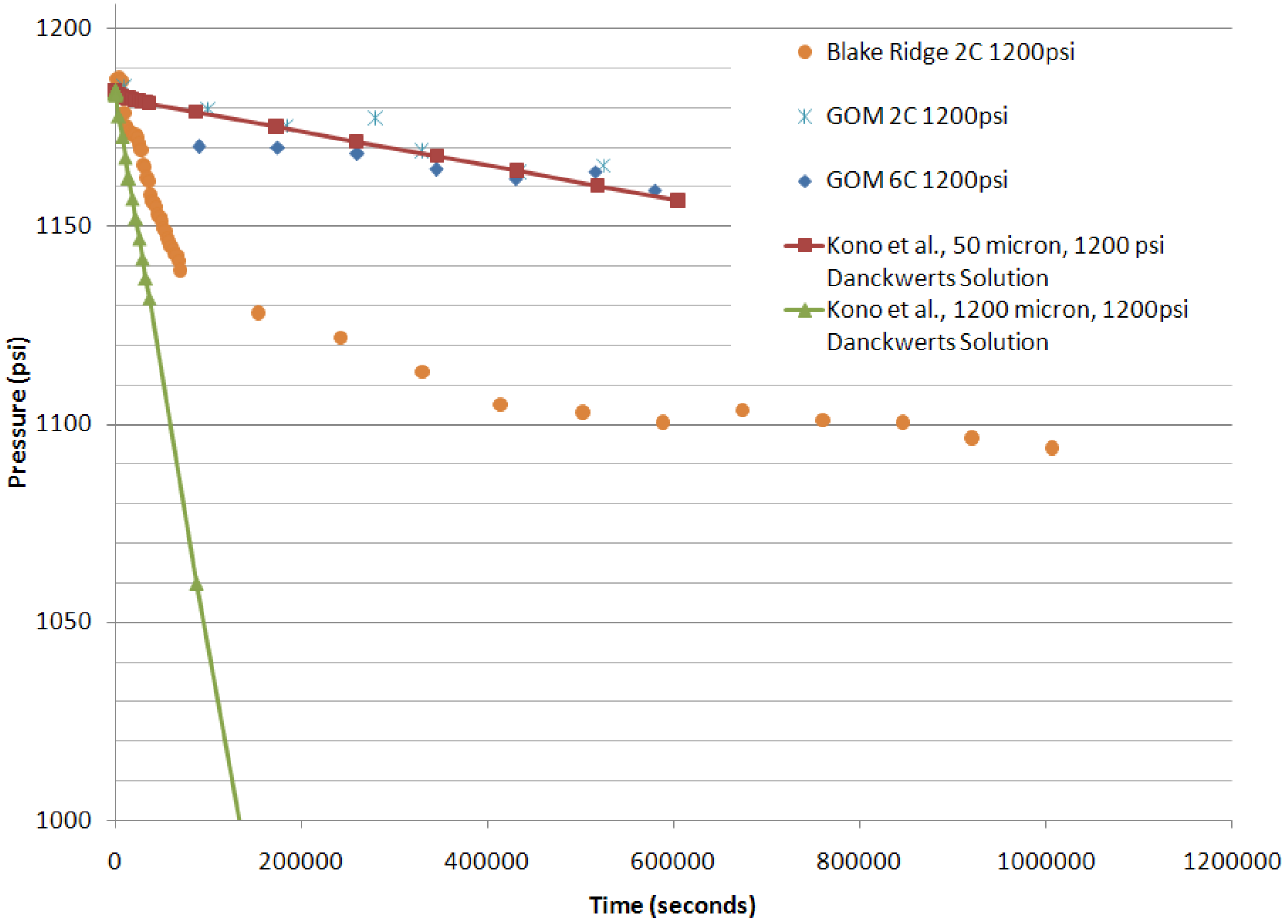


Figure 7. A comparison of pressure drop under 1200 psi methane hydrate formation conditions for GoM and BLR host sediments to theoretical mass-transfer calculations.

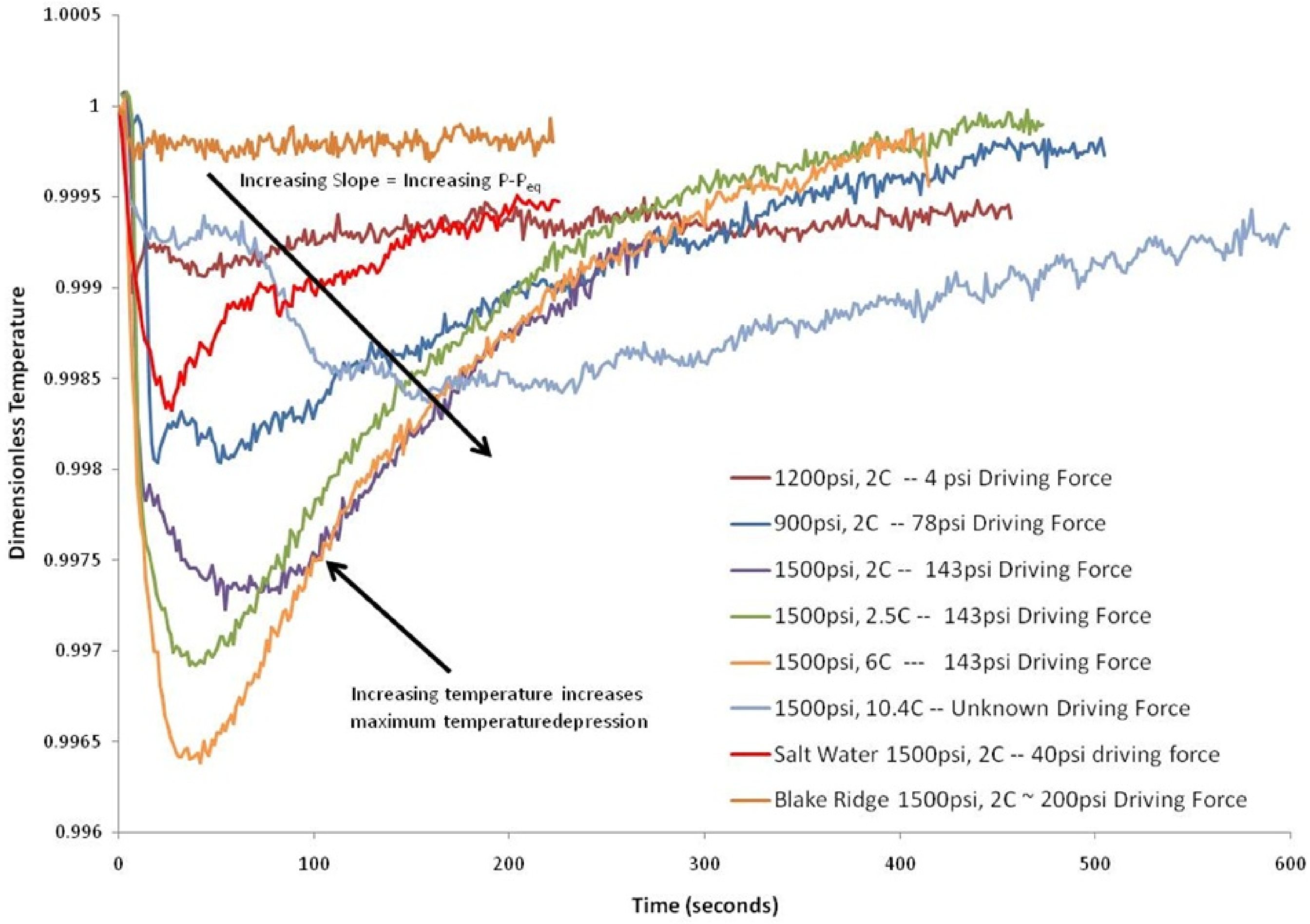


Figure 8. Temperature profiles for hydrate decomposition via depressurization for a range of temperatures, pressures, and fugacity differences.

Task 2.2. Consolidated cores

The Temco DCHR vessel was fitted in the FISH unit (Figure 1) and used to form consolidated cores in Ottawa sand.

Features:

- Vessel volume: 309 mL
- Maximum working pressure: 34 MPa.
- Observation windows: None. An optional camera can be added for *in situ* observation of methane hydrate growth.
- Hydrate type formed: Consolidated
- Forms hydrates in sediment samples from pore water and excess methane gas.

Core formation Conditions:

Core holder: Temco DCHR-2.0 w/ 3 temperature ports (at 1", 3", 5" core length)
Core holder volume: 308.9 mL
Core holder diameter: 2 inch
Core holder length: 6 inch
Sediment: 462.42 gm of Ottawa Sand F110
Average grain diameter– 110 µm (bulk)
Sediment density: 1.625 gm/mL
Volume of two ceramic filters: 24.3 mL
Volume of sand: 284.6 mL
Confining pressure: 1300 psig
Water saturation: ~ 100%
Core temperature: 4^{o}C
CH_4 purity: 99.99%
Methane charging pressure: ~1200 psig.
Charging flow rate: < 2000 mL/min (gradual charge)

Procedure

1. The pressure vessel is placed in the water tank of the FISH unit.
2. The rubber sleeve inside the vessel is totally filled up with dry and weighed sediment.
3. Water is flowed through the sediment sample while pressure is raised. This process attains water saturation.
4. The vessel is pressurized with CH_4 till the desired pressure is attained ($\leq$ 1500 psi). This system (including the vessel) pressure is maintained with a Back Pressure Regulator (BPR).
5. The vessel is cooled to 4^{0}C and maintained.
6. The pressure drop is monitored by a pressure transducer (error: ±1psi) that continuously records the drop in system pressure. The pressure drop is a quantitative measure of hydrate formation.
7. Periodically, CH_4 is charged to the system to maintain set pressure.
8. The process continues till no more CH_4 is consumed- this represents methane hydrate saturation in hosted sediment.

Data Recording

1. The exact amount of consumed/evolved CH_4 is calculated from the total drop in system pressure/flow meter reading during a given run.
2. The Labview records T/P versus time data over the entire run.

Completed Formation and Step-wise Dissociation Runs

After successful completion of four trial runs (first 4 runs in Table 3) with the water/methane/Ottawa sand reference system, a series of four runs were carried out (last 4 entries in Table 3). Two runs were performed at 1200 psig/4°C and two at 1200 psig/2°C. The confining pressure and pressure/temperature conditions were kept identical and the dissociation conditions were varied. The dissociation was achieved with the depressurization technique by dropping the system pressure in 100 or 200 psi (from the hydrate equilibrium pressure) intervals. The pressure, temperature, and gas output parameters were recorded during decomposition. The observations from the collected data are:

- During hydrate formation at 1200 psig/4ºC with 108 mL pore water, it took 60 hours for the pore pressure to asymptote to the equilibrium pressure (Figure 9). Upon recharging, it took 90 hours to equilibrate. The increased time needed for equilibration is due to sluggish rate of formation as more pore water is consumed over time.

- Hydrate dissociation with the depressurization technique resulted in an instantaneous gas output as high as 50 L/min for both 100 and 200 psi pressure drops below the equilibrium pressure (Figures 10 and 11). The cumulative gas produced for various pressure drops is shown in Figure 12.

- The greater the pressure drop during dissociation, the higher the degree of cooling. A longer time period was observed for sediments to reach initial in-situ temperatures (Figure 10).

- The presence of methane hydrate in sediments was confirmed by post-depressurization PT equilibrium that slightly shifted towards higher pressure from the theoretical pure methane hydrate PT stability curve (Figure 13). This is due to the excess pore (48.28 μm) pressure generated during subsequent thermally induced dissociations. The enthalpy of dissociation of methane hydrates was calculated to be 59.134 kJ/mol using the Clausius-Clapeyron equation (Figure 14).

- The pressure drop of 200 psi was enough to completely dissociate methane hydrates formed in confined sediments in all the runs (Figure 11).

- During an endothermic methane hydrate dissociation, the faster temperature drop was at the center (T3) and half-radius (T2) compared to that at the wall (T1) of the core. This observation confirmed that during dissociation, both at 100 and 200 psi, the hydrate front started to dissociate from the center towards the wall (Figure 15).

Table 3. Summary of runs completed to form consolidated cores in Ottawa sand in the FISH unit fitted with the Temco cell*.

Sediment: Ottawa sand F110; Core size: 2" Diameter & 6" Length						
Formation Conditions		**Overburden P**	**CH_4 Charge**	**# Hydrate Formation Events**	**Dissociation Conditions**	**Notes**
P	**T**					
psig	**^oC**	**psig**	**mL/min**			
1200	4	1300	<1950	1	100-200 psi pressure drop below Peqm	Preliminary back-pressure regulator calibration
1200	4	1300	<2000	1	Instantaneous dissociation (w/o back-pressure)	Preliminary run for DAQ
1200	4	1300	<1871	1	100-200 psi pressure drop below Peqm	Another attempt for back-pressure calibration
1200	4	1300	<1718	1	Instantaneous dissociation (w/o back-pressure)	While raising cell pressure from Peqm before dissociation, inlet valve failed!
1200	4	1300	<1916	2	100 psi pressure drop below Peqm	To estimate gas output for each Δp.
1200	4	1300	<1677	2	200 psi pressure drop below Peqm	To analyze effect of Δp on the amount of gas
1200	2	1300	<1594	2	200 psi pressure drop below Peqm	Effect of temperature on gas output.
1200	2	1300	<1759	2	100 psi pressure drop below Peqm	To analyze effect of Δp on the amount of gas at different temperature.

*Run conditions are in the text under Task 2.2.

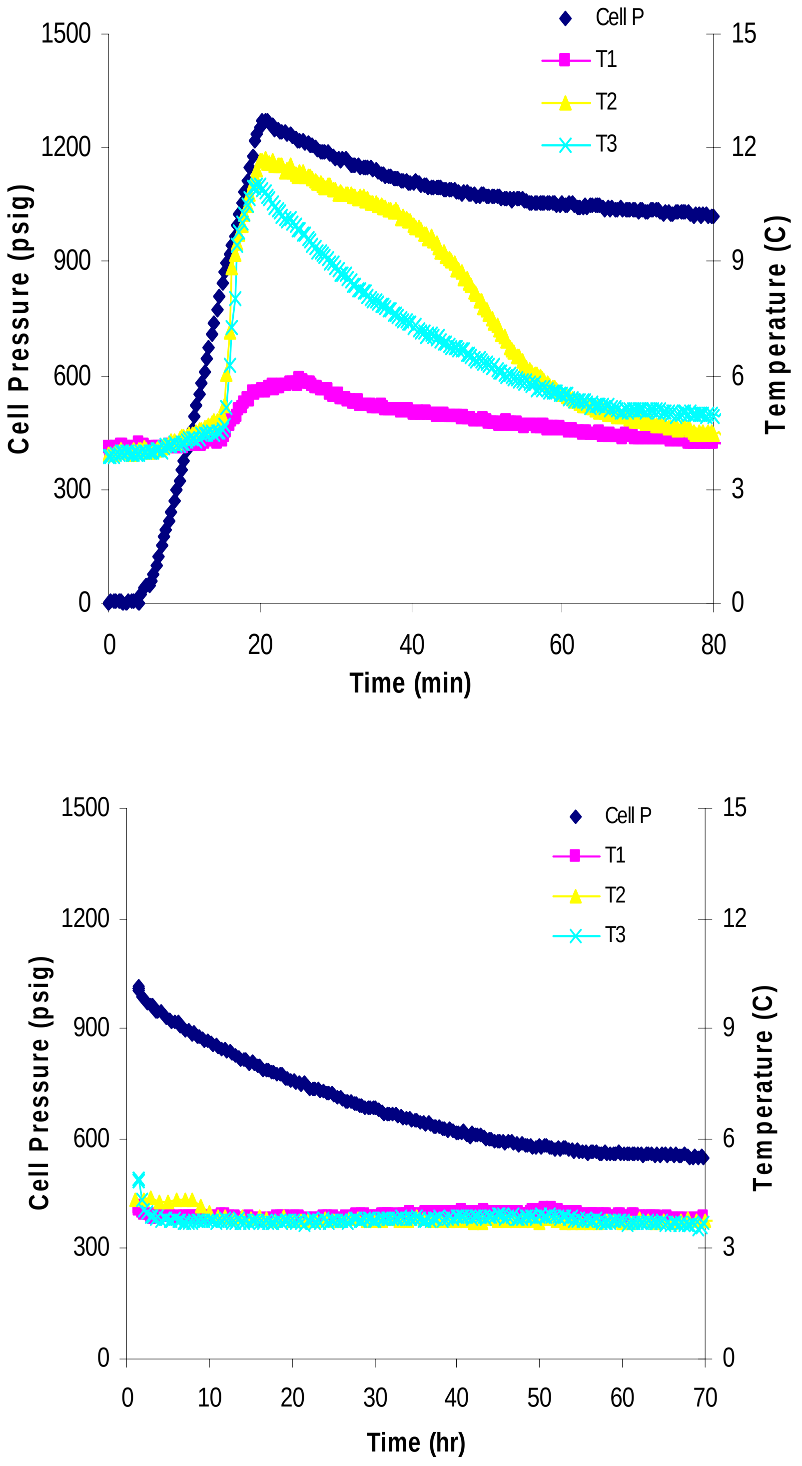


Figure 9. Pressure/Temperature versus time plots during (a) initial charging and (b) first hydrate formation event.

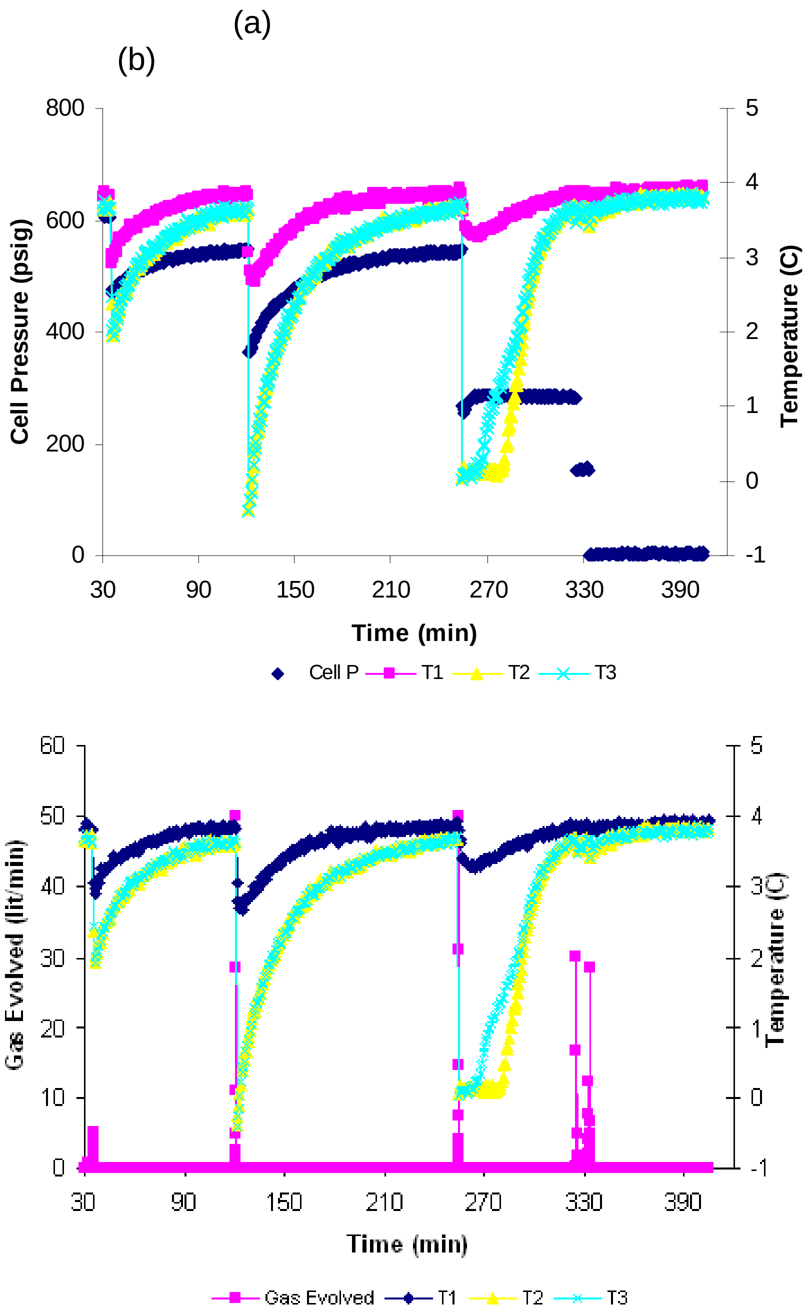


Figure 10. (a) Pressure/Temperature versus time plots and (b) gas evolved during dissociation. The stepwise pressure drop value from equilibrium pressure was 100 psi.

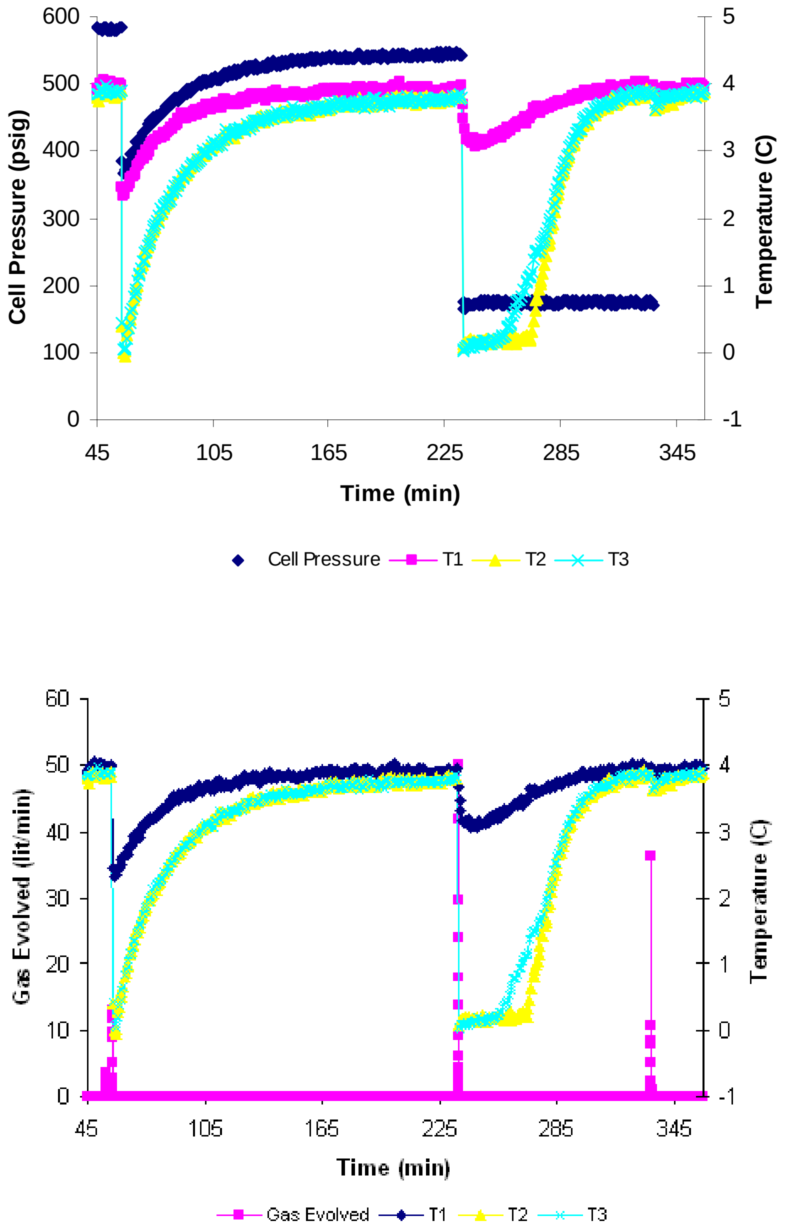


Figure 11. (a) Pressure/Temperature versus time plots and (b) gas evolved during dissociation at 200 psi pressure drop from the equilibrium pressure.

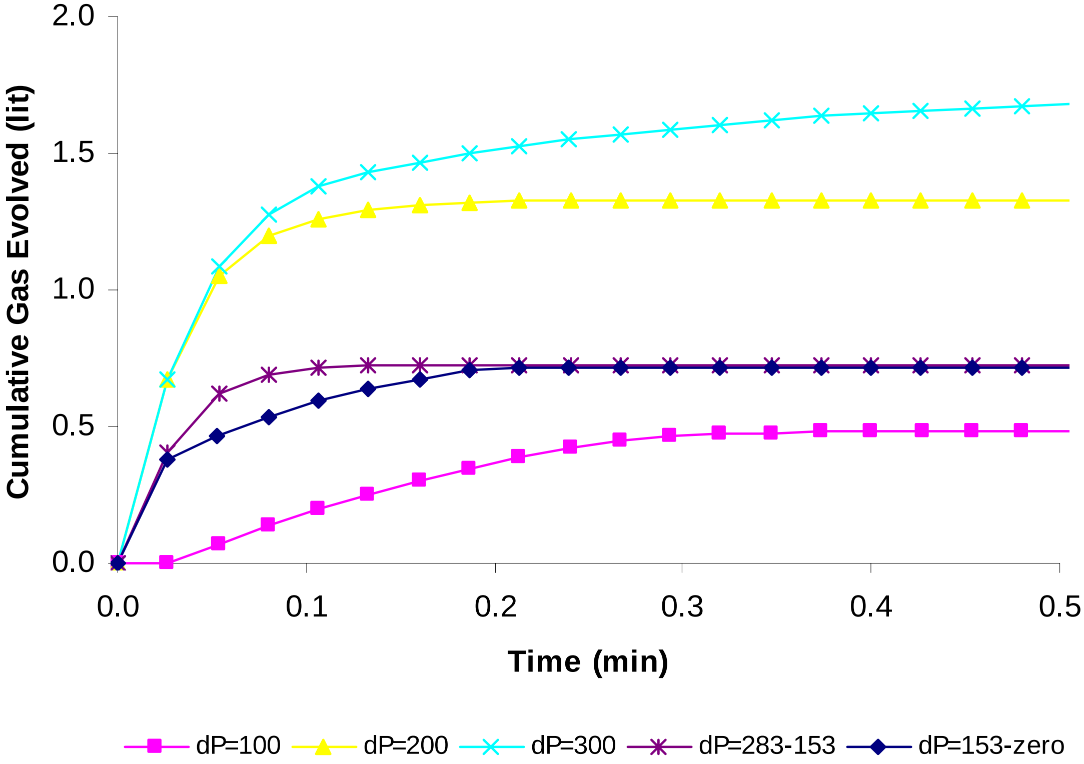


Figure 12. Cumulative gas produced versus time for various pressure drops.

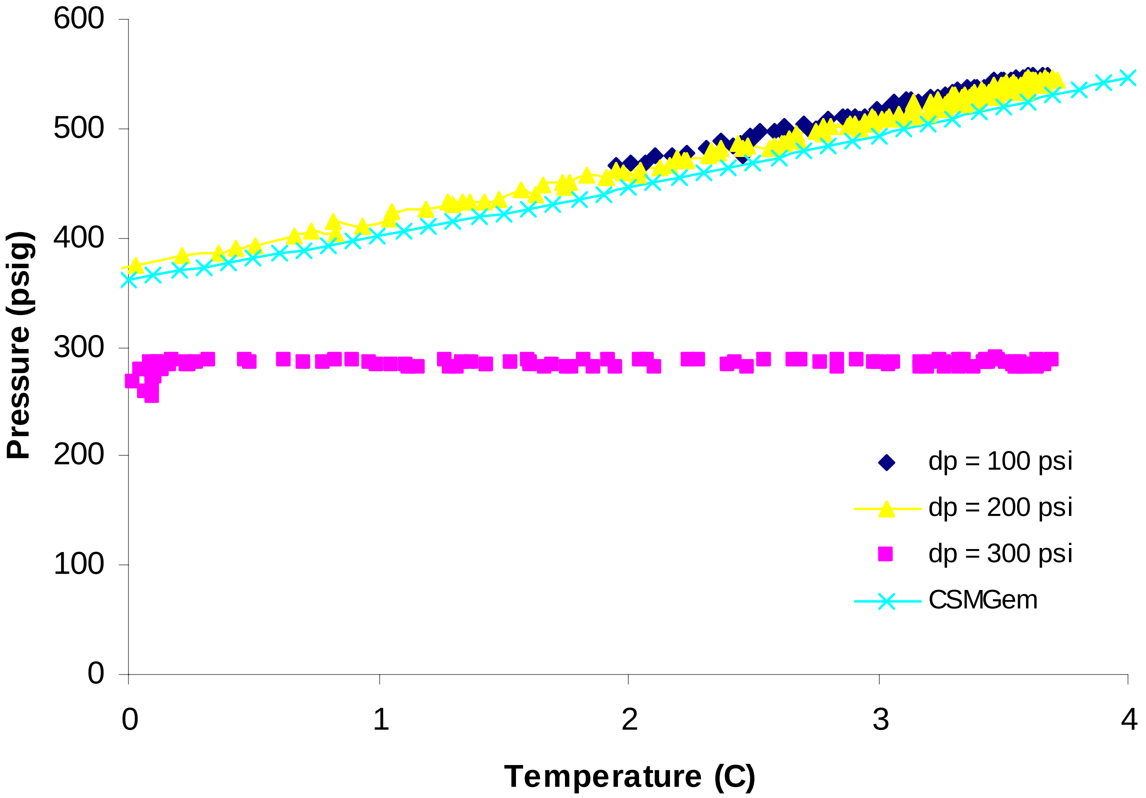


Figure 13. Post-dissociation equilibrium pressure/temperature plots.

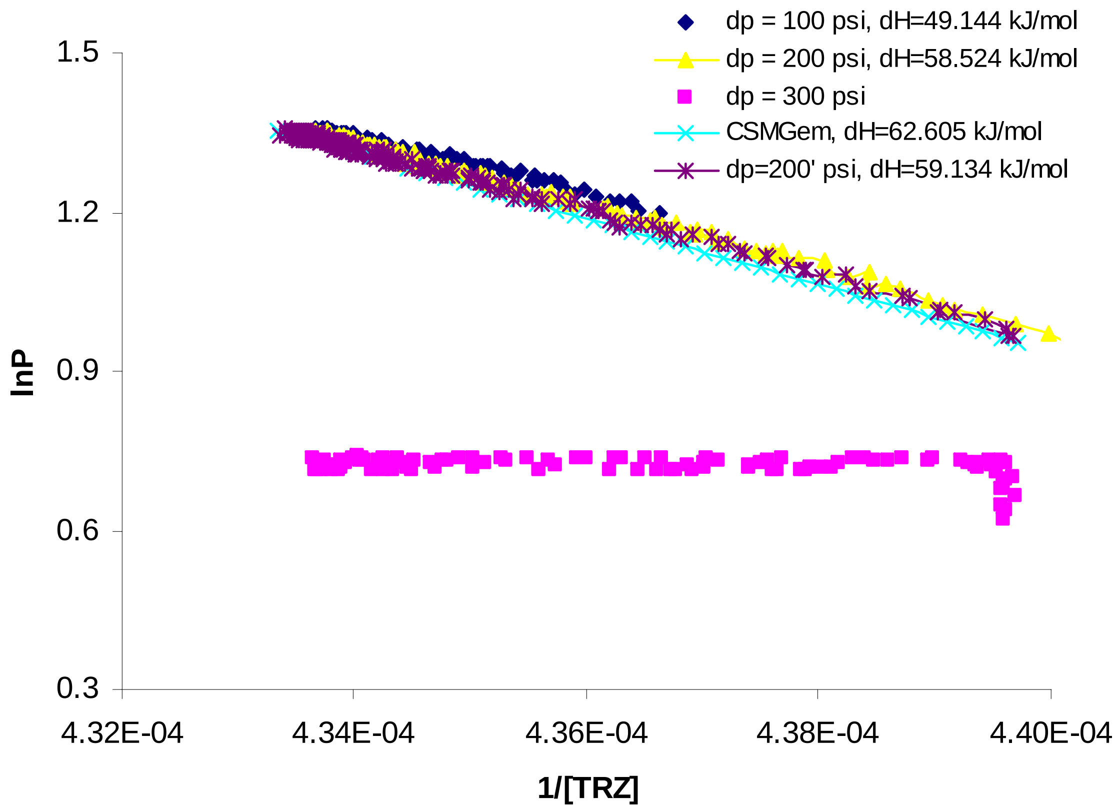


Figure 14. A Clausius-Clapeyron equation plot for post-dissociation PT equilibrium and theoretical PT stability data for pure methane hydrate from CSMGem.

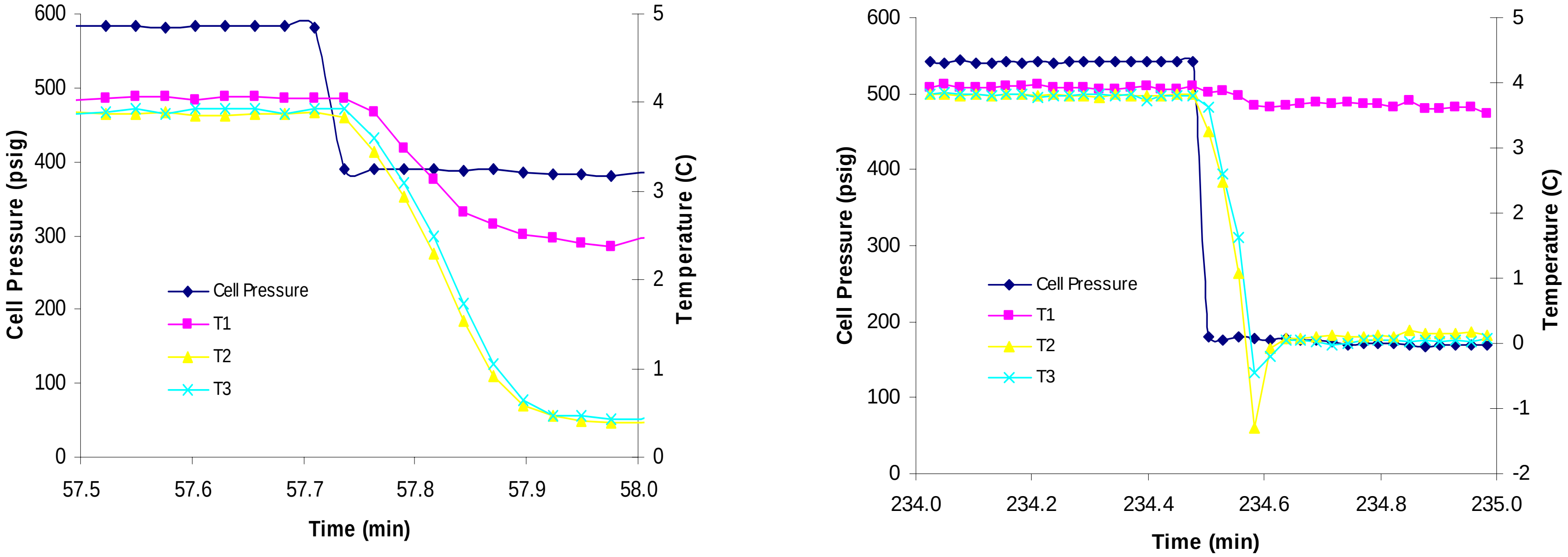


Figure 15. Pressure and core temperature dynamics at various core locations (core center (T3), half-radius (T2), core wall (T1)) during dissociation at 100 psi pressure drop below the hydrate equilibrium pressure.

Task 3. In-Situ hydrtae growth study using CMT

The CMT study was carried out at Beamline X2B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL).

Task 3.1. Data collection and steps to reconstruction and analysis. The collected CMT data at the beamline needed processing to construct 2D and 3D images of the sample. Though image construction methods were available, the process was cumbersome and the data reproducibility was not always obtained. An effort was made to develop a stepwise procedure. The new steps developed were as follows: 1) About 300 slices from each of the .prj files are constructed into a volume file using a routine (convert_x2b_netcdf_display.sav) by Mark Rivers (U. of Chicago) and IDL tomography software. 2) The excess air in the X-direction can be thrown out and all 1200-1800 angular images can be reconstructed with another routine (tomo_display.sav) to get horizontal cross-section of the sample. 3) The vertical axis can be optimized while running tomo_display.sav for each reconstruction to reduce the artifacts in the images. The method was successfully used.

Two natural depleted sediments from 50 and 667 mbsf depths from the Blake Ridge (BLR) site and one from the GoM were characterized using the CMT technique. The data were used to extract porosity and tortuosity values as shown in Table 4. The bulk values are from Winters et al.

Table 4. Porosity and tortuosity values of natural methane hydrate depleted sediments (calculated from the CMT data).

Sample	**BLR-50**	**BLR-667**	**GoM**
Bulk Porosity (%)*	70.0	51.0	**
CMT Porosity (%)	68.6	55.8	**
CMT Tortuosity (%)	1.81	1.89	**

*The bulk values are from Winters et al.

**- Under analysis

Task 3.2. Characterization of THF-hydrate in porous media. To date, a detailed CMT study has been completed with THF-hydrate hosted in glass beads (reference system). The procedure and results are described below.

THF hydrate (Structure II), a surrogate for methane hydrate (Structure I), was studied to determine the feasibility of the CMT technique. The present beamline configuration at BNL was limited to samples at ambient pressure. A 19 wt% THF solution (stoichiometric mole ratio of THF/ H_2O: 1/17) forms Structure II hydrate at ~ 278 K (~ 6°C) and atmospheric pressure. Moreover, the highest economic potential sites from Mississippi Canyon 852/853 (~ 1050-1060 m water depth) in Gulf of Mexico contain hydrate of C1-C5 hydrocarbon gases (Structure II) occur within deformed and gassy sediments containing biodegraded crude oil (*Milkov and Sassen, 2003)*. Thus, THF hydrate, a surrogate for methane hydrate system studied not only determines the feasibility of the CMT technique for proposed study but also provides an advantage of utilizing the present beamline configuration for atmospheric pressure. The sample holder used for preliminary analysis was typical 1 mL polypropylene syringe fitted into a cooling jacket.

We focused on the visualization of hydrate growth phenomena at the micro scale (total volume ~1 mm^3) in a THF/H_2O/$BaCl_2$/glass bead (uniform 500 μm size) system. An aqueous solution containing 25 wt% $BaCl_2$ (saturation limit of $BaCl_2$ in H_2O is 30 g/mL at -3^{o}C) was used to enhance the density contrast between aqueous THF solution and THF-hydrate; it also helpfully lowered the freezing point of the solution to -6.85^{o}C. To initiate THF-hydrate formation, the temperature of the circulating fluid was lowered to -3°C. Hydrate formation was monitored over three days and the resulting data was processed using a multi-step data reconstruction procedure that produced 2-D and 3-D images (Figures 16 and 17). The salient observations from this study are as follows:

- The hydrate formation appears to start at a few locations in the system before the first images were taken at 28 hours. Figure 16 shows the growth pattern of THF hydrate and its interaction with glass beads.

- Time lapse bead-to-bead matching indicates that the growth of hydrates displaces beads within the unconsolidated pack. Further, the 2-D images from the stack show that the hydrate size and shape is independent of container-walls. These observations are consistent with previous NMR (Mork, 2000) and visual observations (Tohidi, 2001) and random nature of the nucleation process.

- The hydrates seem to grow in pores, similar to the pore-filling cementation model described by Dvorkin et al (1999). This implies progressive but significant reduction of mechanical strength of the sediment upon dissociation of hydrates from pore walls by retracting from the pore wall followed by shrinking in the pore space (Kleinberg, 2003).

- The hydrate dissociation from large pores however, will trap gas within pores until hydrate saturation reaches low values and it sustains relative permeability. The 2-D hydrate growth is found convex away from the grains and THF, not hydrate, is the wetting phase in the form of a thin film with thickness < 37 μm. This is analogous to the ice growth in porous media in which a water film remains unfrozen (Kleinberg, 2005) and to the contact angle arguments of Miller (1980) and Clennell (1999).

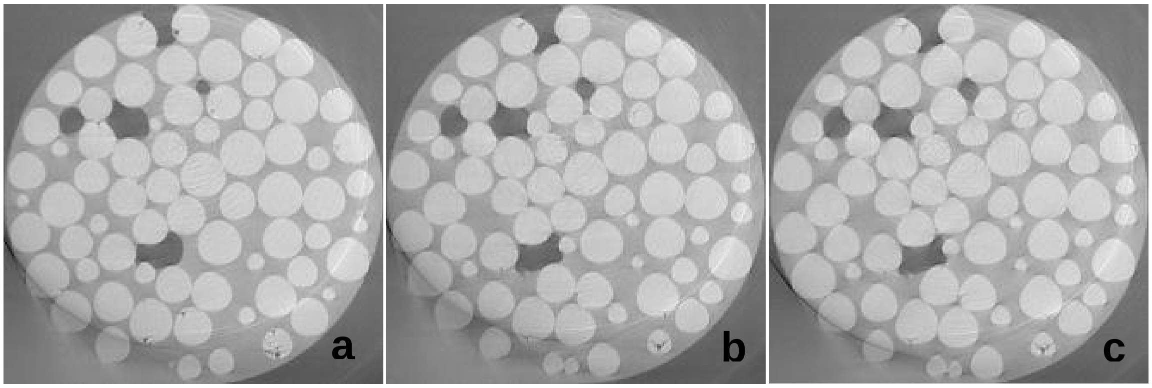


Figure 16. 2-D images of random THF hydrate (black) growth hosted in glass beads (white spheres) in a representative 2-D cross sections (7 mm diameter). The images were recorded at (a) 54 h (b) 70 h and (c) 74 h.

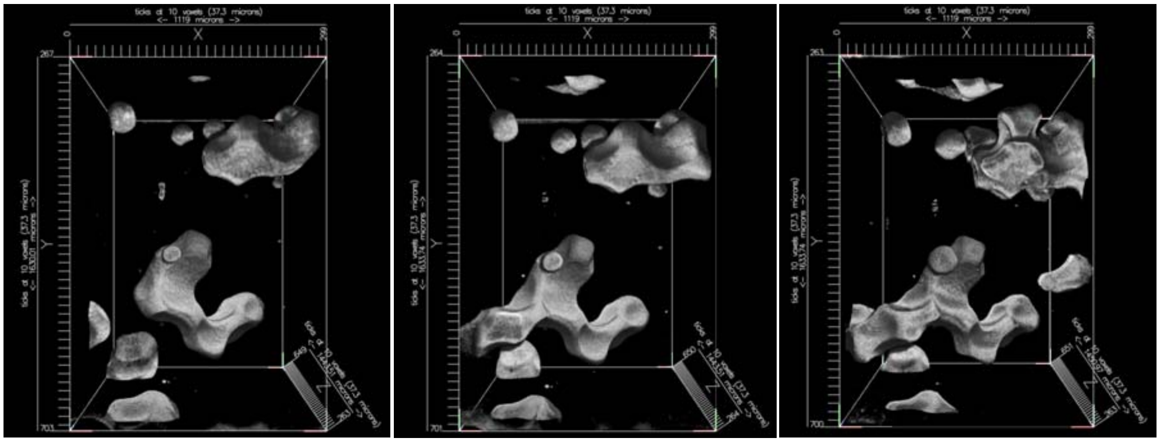


Figure 17. Time resolved THF hydrate growth in glass beads serving as host. The 3-D structures are rendered from tomography scans at cooling times (a) 28:5 h, (b) 54 h and (c) 78:4 h. The glass beads are not shown to allow enhancement of the contrast for distinct observation of THF-hydrate growth (shown in grey scale).

VI. Ongoing and Future Work

VI.1. *In-situ* methane hydrate growth study. This task is focusing on the design and construction of a high-pressure cell of ~10 ml volume that can accommodate the sediment-water mixture at high pressures and low temperatures.

VI.2 Consolidated cores formation in the FISH unit. Replace Ottawa sand with the naturally depleted GoM sediment to mimic naturally occurring marine methane hydrates.

References

- Clennell, M.B., Hovland, M., Booth, J.S., Henry, P., Winters, W.J., Formation of Natural Gas Hydrates in Marine Sediments – Conceptual Model of Gas Hydrate Growth Conditioned by Host Sediment Properties, J Geophysical Res., 104, B10, 22985-23003, October 10, 1999.
- Dvorkin, J., M. Prasad, A. Sakai, and D. Lavoie, Elasticity of Marine Sediments: Rock Physics Modeling, Geophys. Res. Lett., 26(12), 1781-1784, 1999.
- Eaton, M., Kerkar, P. et al., "Methane Hydrate Formation in the Laboratory using Fine Depleted Natural Sediments as Hosts", To be presented at American Chemical Society, Fall 2008 National Meeting and Exposition, Philadelphia, PA, 17-21 August 2008.
- Eaton, M., "Mimicking Marine-based Natural systems: A Study of Sediment-hydrate Interactions Under *in situ* Conditions", Ph.D. Thesis, Stony Brook University, December 2007.
- Ginsburg, G.D., Soloviev, V.A., Proceedings of Offshore Technology Conference, Houston, TX, 1995, 1: p. 513–518.
- Handa, Y.P., Stupin, D., J. Phys. Chem., 1992, 96: p. 8599-8603.
- Jallut, C., Lenoir, J., Bardot, C., Eyraud, C., Thermoporometry: Modelling and Simulation of a mesoporous Solid, J. Membrane Science, 68, 271-282, 1992.
- Kleinberg, R.L., Griffin, D.D., NMR Measurements of permafrost: Unfrozen water assay, pore scale distribution of ice, and hydraulic permeability of sediments, Cold Regions Science and Technology, 42, 63-77, 2005.
- Kleinberg, R.L., Flaum, C., Collett, T.S., Magnetic Resonance Log of Mallik 5L-38: Hydrate Saturation, Growth Habit, Relative Permeability and Control of Accumulation in: S.R. Dallimore and T.S. Collett, Editors, Scientific results from Mallik 2002 gas hydrate production research well, Mackenzie Delta, Northwest Territories, Canada, Bulletin 585, Geological Survey of Canada, Ottawa, 2005.
- Kleinberg, R.L., Flaum, C., Griffin, D.D., Brewer, P.G., Malby, G.E., Peltzer, E.T. and Yesinowski, J.P. "Deep sea NMR: Methane hydrate growth habit in porous media and its relationship to hydraulic permeability, deposit accumulation, and submarine slope stability", Journal of Geophysical Research 108(B10): 2508. doi:10.1029/2003JB002389 (2003).
- Kono H.O., Narasimhan S., Song F., Smith D.H., Powder Technology, 2002, 122 (2-3): p. 239-246.
- Limaye, A., Drishti – Volume Exploration and Presentation Tool, Poster Presentation, Vis 2006, Baltimore, USA.
- Mahajan, D., Taylor, C.E., Mansoori, G.A., eds. J. Pet. Sci. & Eng., 2007, 56 (1-3).
- Mayer, R.P., Stowe, R.A., Packed uniform sphere model for solids: Interstitial access opening sizes and pressure deficiencies for wetting liquids with comparison to reported experimental results, Journal of Colloid and Interface Science, 294, 139-150, 2006.
- Miller, R.D., Freezing phenomena in soils, Introduction to Soil Physics edited by D. Hillel, 254-299, Academic, San Diego, California, 1980.
- Mork, M., Schei, G., Larsen, R., NMR Imaging Study of Hydrates in Sediments, Annals New York Academy of Sciences, 912, 897-905, 2000.

- Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://rsb.info.nih.gov/ij/, 1997-2005.
- Sloan, E.D., Brewer, P., Charter, P., Dutta, N., Johnson, A., Jones, E., Juenger, K., Kastner, M., Mahajan, D., Masutani, S., Swenson, R., Whelan, J., Wilson, S., Woolsey, R., Four Critical Needs to Change the Hydrate Energy Paradigm from Assessment to Production: The 2007 Report to the U.S. Congress by the U.S. Federal Methane Hydrate Advisory Committee (MHAC). 2008 Offshore Technology Conference, Houston, TX, May 5-8, 2008. Paper #: OTC-19519-PP.
- The 2007 Report to the U.S. Congress by the U.S. Federal Methane Hydrate Advisory Committee (MHAC): "Four Critical Needs to Change the Hydrate Energy Paradigm from Assessment to Production".
- Tohidi B., Anderson, R., Clennell, M.B., Burgass, R.W., Biderkab, A.B., Visual Observation of Gas Hydrate Formation and Dissociation in Synthetic Porous Media by Means of Glass Micromodels, Geology, 29, 9, 867-870, 2001.
- Tomov, S. and M. McGuigan, Interactive visualization of higher dimensional data in a multiview environment, arXiv:cs.GR/0405048, May 2004.
- Turner, D.J., Cherry, R.S., Sloan, E.D., Sensitivity of Methane Hydrate Phase Equilibria to Sediment Pore Size, Fluid Phase Equilibria, 228-229, 505-510, 2005.
- Winters, W.J., Waite, W.F., Pecher, I.A., et al., AAPG Hedberg Conference, Sept. 12-16, 2004, Vancouver, BC, Canada.