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Fiber optic sensing technology for detecting gas hydrate formation and decomposition

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A fiber optic-based distributed sensing system (DSS) has been integrated with a large volume (72 l) pressure vessel providing high spatial resolution, time-resolved, 3D measurement of hybrid temperature–strain (TS) values within experimental sediment–gas hydrate systems. Areas of gas hydrate formation (exothermic) and decomposition (endothermic) can be characterized through this proxy by time series analysis of discrete data points collected along the length of optical fibers placed within a sediment system. Data are visualized as an animation of TS values along the length of each fiber over time. Experiments conducted in the Seafloor Process Simulator at Oak Ridge National Laboratory clearly indicate hydrate formation and dissociation events at expected pressure-temperature conditions given the thermodynamics of the CH_4 – H_2O system. The high spatial resolution achieved with fiber optic technology makes the DSS a useful tool for visualizing time-resolved formation and dissociation of gas hydrates in large-scale sediment experiments. © 2011 American Institute of Physics. [doi:10.1063/1.3514983]

I. INTRODUCTION

Gas hydrates are solid, crystalline structures in which water molecules arrange to form polyhedral cages large enough to hold low-molecular-weight molecules at low temperature and modest pressure. Methane hydrates occur in continental margins and terrestrial permafrost sediments where there are adequate sources of H₂O and hydrate-forming molecules, usually alkanes such as methane. Methane hydrates are of interest from both environmental and economic standpoints as a potential source of natural gas, as a reservoir of greenhouse gases, and as a seafloor destabilizing mechanism. Research indicates that hydrates are sensitive to changes in deep ocean conditions such as increases in temperature,¹ have the potential to influence global climate change by sequestering or releasing greenhouse gases,² and are also considered as a potential source of natural gas for human energy consumption.^{3,4} Hydrate samples have been recovered in marine sediments in active and passive ocean margins as well as in subpermafrost sediment providing information on their physical characteristics.^{5–11} Analysis is complicated since natural gas hydrate deposits often exist as disseminated particles formed within a small fraction of pore space over zones tens of meters thick.

A Seafloor Process Simulator^{12–14} (SPS) was developed as a mesoscale apparatus to bridge laboratory scale characterization of gas hydrates and seafloor conditions. The SPS is a 72 1, 20 MPa-capable pressure vessel that is housed in an explosion proof cold room. Most experiments are conducted at ~4 °C, approximately the temperature of the seafloor. The hydrate stability field at this temperature begins at 3.85 MPa. During early experiments, the overall pressure and temperature of the SPS were monitored with thermocouples and pressure transducers.^{15–18} Hydrate formation/dissociation was observed visually using multiple ports with sapphire windows. Recently, a fiber optics temperature-strain (TS) sensing system has been added to observe temperature changes that correspond to gas hydrate formation (exothermic) or dissociation (endothermic) throughout the volume of the system. The optical fibers have Bragg gratings every 1 cm so that each fiber (approximately 2-3 m in length) has around 150-200 gratings matching the spatial scale of gas hydrate occurrences in nature. Fiber optics-based sensing technology has been previously used to continuously measure temperature and strain downhole in monitoring studies of petroleum reservoirs,¹⁹⁻²¹ soils,²² and proposed for monitoring hydrocarbon gases in regions containing gas hydrates.²³ Fiber optic sensors can withstand harsh environmental conditions that conventional pressure sensors cannot.²⁴ In addition to adding spatial resolution, data can be collected at specified time intervals resulting in time-resolved, 3D temperature-strain monitoring. This report describes the fiber optic system specifications, operation, and utility in visualizing gas hydrate formation and dissociation.

II. EXPERIMENTAL DESIGN

In situ experiments were conducted in a 331 polyvinyl chloride (PVC) sediment column with polycarbonate windows placed inside the SPS and cooled to ~4°C for the duration of the experiment (Fig. 1). Commercially available Ottawa sand was sieved to 100–500 μ m. De-ionized water was added to the sand to saturate the pore space to greater than 40% water saturation. The wet sand was placed



FIG. 1. (Color online) Schematic showing the sediment column. Reservoir (A), isolation valve (B), gas diffuser line (C), and optical fiber layers $(D_1, D_2, and D_3)$.

inside the PVC sediment column and layered with three or more data-gathering fiber optics planes with one or two fibers per plane. The optical fibers were connected to the multiplexer/backscatter reflectometer (described in detail below), via a specially designed pass-through port in the wall of the SPS. Two thermocouples, connected through different passthrough ports, recorded temperature in the space between the PVC sediment column and the wall of the SPS. A pressure transducer was used to monitor the overall pressure of the system. The temperature and pressure readings from the thermocouples and pressure transducer, respectively, were recorded using a LABVIEW (National Instruments Corporation, Austin, TX) system.

The distributed sensing system (DSS) is composed of an optical backscatter reflectometer (part No. DSS-80NF) and 2–3 m long and 140 μ m diameter optical fibers (DSS Sensing fibers: OPT03002) with Bragg gratings embedded in the fibers every centimeter. Both the DSS and the germaniumdoped silica core optical fibers were purchased from Luna Innovations (Blacksburg, VA). To help reduce the strain influence on the measurements and increase durability, the manufacturer coated the fibers with Teflon. The temperature and strain resolution can be as small as ± 0.1 °C and $\pm 1 \mu$ strain, respectively. When temperature and/or strain changes occur along the optical fibers, the Bragg grating changes size, affecting the optical properties and the Bragg wavelength of the fiber.²⁵ The individual gratings are read along each 2–3 m fiber by the optical backscatter reflectometer as it sweeps through a range of wavelengths. With changes in the temperature or strain stimulus to the fiber, the return from each grate will vary, indicating that the combination of parameters (temperature and strain) has varied. The temperature and strain changes result in a shift in the resonance wavelength $\Delta\lambda$ or spectral frequency Δv of the Bragg grating:

$$\frac{\Delta\lambda}{\lambda} = -\frac{\Delta\nu}{\nu} = K_T \Delta T + K_\varepsilon \varepsilon, \tag{1}$$

where λ is the mean optical wavelength, ν is the mean optical frequency, and K_T and K_{ε} are the temperature and strain coefficients, respectively. The thermal expansion and thermo-optic coefficients contribute to the temperature co-



FIG. 2. TS values for the four optical fibers recorded at time step 1, 60 s into the experiment (enhanced online). [URL: http://dx.doi.org/10.1063/1.3514983.1].

efficient while the strain coefficient is a function of refractive index, the strain-optic tensor, and Poisson's ratio.²⁶ For the fibers used in this study, the values of K_T and K_{ε} are $6.45 \times 10^{-6} \,^{\circ}\mathrm{C}^{-1}$ and 0.780, respectively. By evaluating Eq. (1) in the absence of strain, the equation becomes

$$\Delta T = \frac{-\lambda}{cK_T} \Delta \nu, \tag{2}$$

where $\overline{\lambda}$ is the center wavelength of the scan and *c* is the speed of light. By evaluating Eq. (1) in the absence of temperature change, the equation becomes

$$\varepsilon = \frac{-\overline{\lambda}}{cK_{\varepsilon}}\Delta\nu.$$
(3)

The optical backscatter reflectometer measures the frequency shift. This frequency shift could be produced by temperature and/or strain changes in the system. If we assume that the frequency shift occurs solely due to temperature change (no strain occurring on the fiber), the y axis of Figs. 2–6 and 8



FIG. 3. TS values for the four optical fibers recorded at time step 40, 40 min into the experiment.



FIG. 4. TS values for the four optical fibers during gas injection. (a) Time step 560, 560 min into the experiment and (b) time step 664, 664 min into the experiment.



FIG. 5. TS values for the four optical fibers after gas injection and during the aging process. (a) Time step 700, 700 min into the experiment, (b) time step 1100, 1100 min into the experiment, (c) time step 1750, 1750 min into the experiment, and (d) time step 2700, 2700 min into the experiment.



FIG. 6. TS values for the four optical fibers toward the end of the aging process at time step 3000, 3000 min into the experiment.

represents a range of ΔT from -5 to 75 °C. If the change in frequency is produced purely by strain (no change in temperature), the range of the y axis would be -4.13×10^{-5} to 6.2 $\times 10^{-4}$. However, in our experiments, both temperature and strain affect the fibers; therefore, we interpret the frequency shift as a hybrid temperature-strain value by using Eq. (1). For the purposes of our studies, the relative change in TS is of principle interest rather than the absolute value. Since gas hydrate formation and dissociation within the sediment affects both temperature and strain around the fiber, the DSS is especially useful in monitoring changes in the system and recording where and when hydrate formation and dissociation occurs within the vessel.

To avoid bending the fibers at sharp angles, which would introduce strain effects, fibers were attached to round plastic mesh grids with fine plastic line in an Archimedean spiral configuration where each revolution maintains a constant separation. Within the spiral configuration, the higher numbered sensors (\sim 150+) corresponded to locations in the center of the sand column. Sensors in the middle range (\sim 50–150) were along the outer areas of the sand column, while the lowest numbered sensors (\sim 1–50) would be going down the vessel wall to the fiber plane. Consequently, two sensors with close angular relationships but different radii will record a temperature event over some discrete area in the vessel producing two peaks in TS readings when the data are plotted in a linear fashion. To differentiate sensors traveling down the vessel wall from those on the sensing plane, ice was placed on the edge of the plane prior to experiments. A low TS value indicated the first sensor on the plane; as a result, the TS values shown are only those that are on the plastic mesh planes.

When eight fibers (two fibers on each sensor plane) with approximately 200 sensors on each are used in an experiment lasting 72 h with data collected every 60 s, approximately 7×10^6 data points are obtained. Such massive data sets were difficult to interpret and analyze in detail. Pressure-temperature (P-T) data from the thermocouples and the pressure transducer were collected and

recorded with LABVIEW every minute, the software provided by LUNA (written in LABVIEW) also recorded the output of the optical backscatter reflectometer every minute. Data analysis was performed with EXCEL and python extensions such as matplotlib (a python plotting module), then animated.²⁷

The sediment column, shown in Fig. 1, was filled using chilled sand mixed with chilled water and layered with fiber planes. The first fiber plane (D_3) was located approximately 5 cm above the bottom of the column and below the diffuser where gas was injected. The diffuser was located approximately 10 cm above the bottom of the column and consisted of a 2.54 cm diameter PVC tube with narrow slots every 6 mm along 10 cm of its 15 cm length. The next two fiber planes were located above the gas diffuser at approximately 15 cm (D_2) and 25 cm (D_1) above the bottom. With this configuration, TS values below the diffuser and at different heights above the diffuser could be compared. The total depth of the sand column was approximately 28 cm. Every plane contained two fibers placed in parallel spirals; however, due to equipment malfunction, only the 5 cm plane recorded data from both sensors. The sediment column was placed in the SPS and a stainless steel reservoir, designed for initially accumulating the CH₄ gas and subsequently replacing the gas with a hydrate inhibiting liquid thereby pushing the gas into the sediment column, was placed on top of the sediment column. The SPS was sealed and placed within the cold room. The system was flushed with nitrogen before pressurizing. The system was flushed again with methane and pressurized to 3.3 MPa (485 psi) with methane. In order to saturate the water with gas, the system remained pressurized with CH₄ overnight. CSMHYD,²⁸ a software package developed at Colorado School of Mines that predicts the thermodynamics of stable hydrate structures as various pressure, temperature, and composition conditions, was used to check that the system was outside the hydrate stability field at the overnight pressure and temperature conditions. After about 20 h, the pressure was increased to just below the hydrate stability field ~ 4.0 MPa (575 psi). During this initial pressurization of the SPS, the reservoir was open to the SPS headspace to equalize the pressure between the two vessels. An inlet into the reservoir allowed a hydrate inhibiting H₂O/methanol (3% methanol) mixture to be introduced from a high pressure liquid chromatography (HPLC) pump. After initial pressurization, the optical fibers were reset, the reservoir was opened to the HPLC pump, and the connection to the SPS headspace was closed. The SPS pressure was slowly increased by pumping the H₂O/methanol mixture into the reservoir system. As the HPLC pump pushed fluid into the reservoir, methane gas was displaced from the reservoir and forced through the diffuser into the sand column. The HPLC pump was operated at less than 8 ml/min to control the rate of methane injection. This slow rate allowed for the difference in pressure between the SPS and the reservoir to remain below 138 kPa (20 psi), under half of the reservoir's burst pressure. The H₂O/methanol mixture was intended to prohibit hydrate formation within the reservoir. Care was taken to avoid overfilling the reservoir so that the methanol mixture did not contact the sediment in the experiment. After approximately 11 h of slow pressurization,

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| Condition | Pressure (MPa) | Temperature (°C) | Free volume (cm ³) | Calculated moles CH ₄ | Estimated hydrate mass (g) |
|-----------------------|----------------|------------------|--------------------------------|----------------------------------|----------------------------|
| Prior to injection | 4.0 | 4.6 | 53 440 | 91.6 | 0 |
| End of injection | 4.4 | 3.9 | 48 518 ^a | 92.8 | 970 |
| Prior to dissociation | 4.2 | 3.6 | 48 518 | 89.6 | 1360 |

TABLE I. Experimental conditions prior to injection, at the end of injection, and prior to dissociation.

^aCalculated from the previous free volume minus the 4882 ml of H₂O/methanol mixed injected using the HPLC pump.

the SPS system was isolated from the pump and left at pressure and temperature for approximately 61 h before depressurization.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The data were initially evaluated using a time lapsed movie of TS values versus sensor number for the optical fibers. The time lapsed movie allowed 5946 frames collected over \sim 99 h to be viewed in \sim 10 min. Figure 2 shows the TS values recorded at time step 1, 60 s into the experiment corresponding to conditions (P = 3.96 MPa and T = 4.6 °C) below the hydrate stability field. Plotted data start at the approximate cutoff for the sensors going down the wall of the sand column and the beginning of sensors located on the horizontal planes. The TS values from plane D₃ remained constant during pressurization and throughout the duration of the experiment, suggesting insignificant hydrate formation occurred below the gas introduction point. The noise seen in the data from the fiber located 25 cm (plane D_1) from the bottom may have been related to the strain influence of the stainless steel reservoir vessel resting on top of the sediment column and interactions with gas in the headspace of the SPS.

Within the first 40 min, the TS values for plane D₂ showed no noticeable increase; however, the D₁ plane showed the emergence of two TS peaks: the higher magnitude peak was centered around sensor 105 and the other centered close to sensor 130 as shown in Fig. 3. These TS peaks suggest hydrate formation near the top of the sand column within 20 kPa (P = 3.98 MPa and T = $4.3 \degree C$) of the predicted hydrate stability field for the experimental temperature where the wet sand was in contact with the methane-filled headspace. Similar observations were made by McCallum et al.15 who attributed the lower over pressures needed for hydrate formation in the SPS resulted from some combination of the increased surface area and lifetime of the gas bubbles, the increased gas concentration, and/or the large volume of the SPS. In other experiments (data not shown), evidence of methane hydrate formation normally appears within 7-28 kPa of the predicted methane hydrate stability field.

Between 40 and 560 min, the TS values for the fiber located 5 cm above the gas diffuser evidenced three peaks centered around sensors 80, 135, and 155 as shown in Fig. 4(a). Figure 4(a) also shows a large magnitude TS peak for the top optical fiber centered around sensor 100. These observations indicated continuing methane hydrate accumulation above the gas diffuser. After 560 min, the TS values for the fiber 5 cm above the gas diffuser rapidly began to grow and converge into one peak centered close to sensor 115 and at the same time the TS values for the optical fiber closest to the top began to decrease in magnitude. These observations are illustrated graphically in Fig. 4(b) showing the data collected at 664 min after the start of the methane injection. The overall vessel headspace temperature remained constant $(4.23 \pm 0.35 \,^{\circ}\text{C})$ while pressure varied from 3.96 to 4.41 MPa (574–639 psi) during the process of injection. These TS results indicate continued hydrate accumulation in the region above the gas diffuser and perhaps small accumulations at the top of the sand column.

The gas injection ceased at 665 min after which the vessel maintained temperature $(3.75 \pm 0.15 \,^{\circ}\text{C})$ and pressure (4.3 \pm 0.1 MPa) for an additional >3000 min. Figure 5(a) shows that after about 700 min the magnitudes of the TS peaks for both of the optical fibers above the gas diffuser were approximately equal in magnitude and this condition persisted for \sim 100 min. After 800 min, the magnitude of the TS peak for the optical fiber located 5 cm above the gas diffuser began to decrease and Fig. 5(b) shows that after 1100 min, the TS peak had decreased significantly and the peak initially centered about sensor 125 has shifted to lower sensor numbers (two small peaks centered at approximately sensors 100 and 120), indicating hydrate accumulation nearer the column wall. Figure 5(c) shows the TS values at 1750 minutes where the peaks have continued to grow and shift closer to the wall. These peaks continued to grow in magnitude and split into two distinct peaks, one centered just below sensor 75 and one centered around sensor 100 as shown in Fig. 5(d). Around 3000 min, these peaks have merged and the magnitude of the peak has increased considerably as shown in Fig. 6. The TS peak for the sensor nearest to the top of the sand column



FIG. 7. TS values for the four optical fibers after depressurization at time step 4270, 4270 min into the experiment.



FIG. 8. TS values for the four optical fibers recorded at (a) 755 min and (b) 756 min into the experiment.

was approximately constant after 664 min up to 1100 min and then can be seen gradually decreasing in intensity. The intensity of the TS values for this peak continues to decrease until 2700 min. At 3000 min, it appears that this peak is beginning to increase again. The TS results from the top optical fibers indicate that during the aging process (without gas input) hydrate accumulation occurred above the gas diffuser and closer to the column wall than the center of the column.

The pressure, temperature, and free volume conditions in the SPS have been summarized in Table I along with the moles of methane calculated using the idea gas law.

Using the ideal gas law along with the pressure and temperature values recorded at the end of injection and the volume equal to that of the H2O/methanol injected approximately 9.3 mol of CH₄ are estimated as added to the system. Adding this to the number of moles of CH₄ prior to injection suggest that 100 mol of CH₄ was present at the end of injection. The difference between this expected amount (100 mol of CH₄) and the observed 92.8 mol of CH₄ indicates that approximately 8.1 mol of CH₄ was consumed, making close to 970 g of hydrate during the injection period of the experiment. During the aging, about 3.2 mol of additional CH₄ was consumed, suggesting that another 390 g of methane hydrate was formed during this period, resulting in a total of approximately 1360 g of hydrate formed. Some methane hydrate could have formed in the H₂O that surrounded the sediment column; however, the TS values discussed earlier support methane hydrate formation and accumulation in the sediment column.

After 4200 min, the SPS was depressurized to below the hydrate stability zone, and the TS values of the top two planes $(D_1 \text{ and } D_2)$ rapidly decreased and returned to values similar to those recorded 1 min after the injection began. This is shown in Fig. 7.

Periodically throughout the experiment, all the fibers would exhibit a data aberration. TS values fluctuated along the fiber, likely indicating strain effects from hydrate formation. Figure 8 compares the data collected at 755 and 756 min

after the start of injection. At 755 min after the start of injection, the curves generated from all the sensors along each fiber are relatively smooth in contrast to the data collected at 756 min that show a larger aberration. The effect persisted for approximately 20 min and was similar to other discrete events observed during the course of the experiment.

IV. CONCLUSIONS

The results in this paper demonstrate that fiber optics sensing technology is a viable way of detecting gas hydrate formation within sediments. The high spatial resolution of the Bragg gratings allows the location of hydrate formation and growth to be monitored throughout the sediment column. In addition, dynamic hydrate growth can be observed through time-resolved, 3D visualization of the TS data. These attributes combine to make DSS an integral tool for centimeter– meter scale studies of gas hydrate in the laboratory and potentially in the field. Future experiments are necessary to assess the effect of the fiber planes providing preferential formation pathways, detection limits of the DSS system, and advanced data visualization capabilities. New methods may also be developed to investigate and understand the data aberrations that appeared during the experiment.

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