straightforward and their correlation, in turn, must be evaluated in the context of the type and scale of the in situ measurement. Resistivity and velocity logging methods are used most often for this purpose. The dissociation of hydrate or the change in free gas concentration in the vicinity of a borehole due to the drilling process may significantly alter these measurements and the correction or quantitative evaluation of the results is usually required. To minimize such effects, LWD logging methods provide higher quality data, but the application of this new technology must be carefully interpreted for the particular host sediment in which gas hydrate may be present.

The measurement of in situ properties using logs is primarily useful for: (1) the identification of hydrate and hydrate-bearing sediment and their distribution with depth, (2) the estimation of porosity and methane saturation, and (3) the calibration on of drill hole information with surface seismic or other remote geophysical data. The table below generalizes the expected response of several common logging measurements in massive hydrate, hydrate-bearing marine sediment, and gas- and water-saturated marine sediments based on the field examples discussed above.

<table>
<thead>
<tr>
<th>Massive Hydrate*</th>
<th>Hydrate-bearing Sediment</th>
<th>Water-saturated Sediment</th>
<th>Gas-bearing Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_p$ (km/s)</td>
<td>3.2-3.6</td>
<td>1.7-3.5</td>
<td>1.5-2.0</td>
</tr>
<tr>
<td>$V_s$ (km/s)</td>
<td>1.5-1.7</td>
<td>0.4-1.6</td>
<td>0.75-1.0</td>
</tr>
<tr>
<td>$R$ (Ω·m)</td>
<td>150-200</td>
<td>1.5-175</td>
<td>1.0-3.0</td>
</tr>
<tr>
<td>$\rho$ (g/cm³)</td>
<td>1.04-1.06</td>
<td>1.7-2.0</td>
<td>1.7-2.0</td>
</tr>
<tr>
<td>$\phi$ (%)</td>
<td>20-50</td>
<td>35-70</td>
<td>35-70</td>
</tr>
<tr>
<td>$\gamma$ (API)</td>
<td>10-30</td>
<td>30-70</td>
<td>50-80</td>
</tr>
</tbody>
</table>

Table 1. Common ranges of in situ log properties *(modified from Mathews, 1986).

In general, resistivity logs typically have high values relative to seawater-saturated sediment as hydrate forming in open pores replaces the more electrically conductive seawater. Both compressional and shear velocity logs typically increase because hydrate acts as a high-velocity pore filling material and as an intergranular cement, stiffening the bulk compressibility and rigidity of the sediment. Sonic log and VSP velocities tend to decrease in the presence of free gas. Natural gamma ray, neutron porosity, and bulk density logs show little or no apparent decrease in hydrate-bearing sediments. In the future new logging and LWD technologies measuring in situ resistivity, velocity and porosity, all of particular importance for detecting gas hydrate occurrences, will provide greater certainty for many of these key parameters.

Chapter 24

GHASTLI - Determining Physical Properties of Sediment Containing Natural and Laboratory-Formed Gas Hydrate

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1. INTRODUCTION

Gas-hydrate samples have been recovered at about 16 areas worldwide (Booth et al., 1996). However, gas hydrate is known to occur at about 50 locations on continental margins (Kvenvolden, 1993) and is certainly far more widespread so it may represent a potentially enormous energy resource (Kvenvolden, 1988). But adverse effects related to the presence of hydrate do occur. Gas hydrate appears to have caused slope instabilities along continental margins (Booth et al., 1994; Dillon et al., 1998; Mienert et al., 1998; Paull & Dillon, Chapter 12; Twichell & Cooper, 2000) and it has also been responsible for drilling accidents (Yakushev and Collett, 1992). Uncontrolled release of methane could affect global climate (Chapter 11), because methane is 15-20 times more effective as a greenhouse gas than an equivalent concentration of carbon dioxide. Clearly, a knowledge of gas-hydrate properties is necessary to safely explore the possibility of energy recovery and to understand its past and future impact on the geosphere.

Gas hydrate exists in the natural environment at pressure and temperature conditions that make it difficult to study in situ. For that reason, the U.S. Geological Survey's Woods Hole Field Center developed a laboratory system (GHASTLI - Gas Hydrate And Sediment Test Laboratory Instrument) to simulate natural conditions within the gas-hydrate-stability region. Using this system, gas hydrate can be formed in reconstituted sediment (Winters et al., 2000) and field samples containing gas hydrate can be preserved (Winters et al., 1999) while physical properties are measured.

GHASTLI determines a number of properties of the host sediment prior to gas-hydrate formation, after hydrate has formed, and after dissociation. Currently, four main types of data are measured: (1) acoustic properties (both compression-wave and shear-wave), (2) shear strength and related engineering
properties under triaxial test conditions, (3) permeability, and (4) electrical resistivity. These results are used to model and predict the relation between the natural environment, sediment fabric, and the existence of gas hydrate.

Acoustic properties can dramatically change as gas hydrate forms, and this relationship allows remote identification of hydrate. Initial velocities derived from seismic data have been used to quantify the presence of gas hydrate (Lee et al., 1993). This acoustic relationship then has been used as a means of mapping the extent of hydrate and may be a means of estimating resource potential. Also, acoustics have been used to model gas-hydrate interaction with host sediment (Dvorkin and Nur, 1993; Pecher et al., 1999). Currently, a number of theories exist that relate the effect of natural gas-hydrate saturation to acoustic behavior, but testing of these theories has not been possible without a laboratory system capable of simulating in situ conditions. Berge et al. (1999) showed that velocity behavior changes occur when pore-volume saturation exceeded about 35% using sand and R11 (CCl₃F) refrigerant as the hydrate former. It is not yet known if hydrate formed with R11 exhibits behavior similar to natural gas hydrate.

Sediment strength properties can be affected by the presence of gas hydrate, however, measurements of the effects of hydrate on sediment strength are scarce. There is currently concern that offshore drilling in the Ormen Lange gas field in the North Sea could dissociate existing gas hydrate and cause seafloor instabilities (Offshore, 2000). The nearby Storegga slide, which caused tsunamis to impact both Scotland and Norway about 7,000-8,000 ka, is thought to have been influenced by gas-hydrate dissociation. Concerns exist that gas-hydrate dissociation related to mass wasting may release methane, a potent "greenhouse gas", to the atmosphere (Chapter 11). A better understanding of strength properties can be used in stability calculations of: (1) natural slopes (Kayen and Lee, 1991), (2) structures placed on land or the seafloor (pipelines and drilling platforms), and (3) wells drilled to recover natural gas and oil (Briaud and Chaouch, 1997).

Sediment permeability is reduced if significant amounts of gas hydrate occupy intergranular pore space. The changes that are produced are important for slope-stability calculations (Kayen and Lee, 1991) and in determining if gas hydrate can effectively form a seal that traps bubble-phase gas beneath the gas-hydrate-stability zone (GHSZ). The presence of gas beneath the GHSZ is a major contributor to the formation of a bottom-simulating reflector (BSR) present on seismic-profile records.

Because electrical resistivity of gas hydrate is much higher than naturally-existing pore water, measurement of that parameter can be used to indicate when gas hydrate has formed in the laboratory and can be used as a comparison to well-logging measurements. Well logging has provided much information about the presence and properties of gas hydrate in the natural state, for example, Collett et al., 1984, 1999; Collett & Ladd, 2000; and Miyairi et al., 1999. Gas-hydrate saturation has also been calculated from well-log information (Lee and Collett, 1999).

Gas hydrate exists naturally in different materials and under varying environmental conditions. Understanding the factors responsible for hydrate formation, preservation, and concentration may enable prediction of locations where methane from gas hydrate can be economically and safely recovered. GHASTLI provides a means for making measurements related to the above topics under conditions that can be closely controlled. Sediment grain size, specimen bulk density, effective stress, and pore-fluid characteristics can be varied to assess their impact on gas-hydrate formation and behavior.

2. GHASTLI

2.1. Overview

GHASTLI combines a number of separate-pressure-and-temperature-control systems (Fig. 1) to simulate in situ conditions on a 71-mm diameter by 140-mm high right-circular sediment specimen (Fig. 2). The 25 MPa pressure (equivalent to the pressure exerted by a 2,500 m column of water) and temperature (25°C to about -3°C) capabilities of the system provide wide latitude in test configurations and procedures within which gas hydrate can be studied in reconstituted sediment or in field samples containing natural gas hydrate. Instrumentation packages and sensors placed within the different subsystems and in close proximity to the test specimen produce measurements that are logged and displayed by a computer running custom-designed software (Fig. 3). During testing, the sample resides within a silicone-oil filled, main pressure vessel (Figure 1). Separate internal sediment pore pressure and external confining pressure systems are used to adjust isotropic consolidation stress, \( \sigma_c \), to simulate in situ overburden pressure.

![Figure 1: GHASTLI system showing the syringe pumps that control pressure and the main pressure vessel, located just to the right of center in the photo, that contains the sediment test specimen.](image-url)
Five 500 ml capacity syringe pumps are used to maintain the confining pressure surrounding the specimen and the internal specimen pressures which include: pore pressure, back pressure, and methane-gas pressure. Flow rates of 0.001 ml/min to over 80 ml/min are controlled by the syringe pumps to a maximum pressure of 25 MPa. The back-pressure system contains a collector that is capable of separating and measuring water and gas volumes that are pushed out of the specimen at test pressures by the dissociation of gas hydrate. A separate syringe pump controls the movement of the load ram during shear tests and is used to determine the height of the specimen (which may change during a test) to increase the accuracy of acoustic-velocity measurements. Four thermocouples and four thermistors are placed against the outside perimeter of the specimen at different heights to measure temperature variations during cooling or warming stages and during gas-hydrate formation and dissociation events.

Because we can reduce specimen temperatures below freezing, ice formation is possible either alone or within the sediment pores. This is important because some physical properties of gas hydrate and ice are similar (Kuustra et al., 1983; Miyairi et al., 1999) and gas hydrate is present in regions where permafrost is present (Dallimore and Collett, 1995; Collett, 1993).
2.2. Acoustics
P-wave velocity is measured by through transmission using 500 kHz or 1 MHz (natural frequency) wafer-shaped crystals that are located on the back side (away from the specimen) of each end cap. A pulser sends an electrical signal, with a 400 volt pulse height, to the transmitting transducer. The received signal typically has a 200 kHz frequency and is amplified, digitized, displayed on a digital oscilloscope, and recorded by a computer. Acoustic compression-wave and shear-wave velocities, \( V_p \) and \( V_s \), are calculated from the specimen length/measured travel time corrected for system delays.

2.3. Strength
Four parameters are measured during triaxial strength tests (Holtz and Kovaes, 1981): load, axial deformation, confining pressure, and pore pressure. Loading is produced by a syringe-pump-controlled ram contacting the heat exchanger which then pushes on the sample at a rate related to the syringe-pump-piston travel. Movement of the ram, which can vary from 0.0001 mm/min to 2 mm/min, is measured using a linear displacement transducer connected to the load ram. Interchangeable load cells can be varied according to anticipated strength of the sediment and gas hydrate.

2.4. Hydraulic conductivity
Hydraulic conductivity measurements are performed (according to procedures in ASTM D 2434-68 (1998), modified for use with syringe pumps) at different phases of testing by flowing water from the bottom end cap up through the specimen and out the top end cap into a back pressure silicone oil/seawater interface chamber. Both constant flow rate and constant head methods are used. Pressures, flow rates, and fluid volumes are recorded from the syringe pumps, and the pressure drop through the specimen is measured with a variable-range differential-pressure transducer or by comparing pressure differences between syringe pumps.

2.5. Electrical resistivity
Four equally-spaced electrical-resistivity probes are placed on opposite sides of the sample. A current is flowed through the outer probes, and the potential is measured between the inner probes at specified times. The direction of current flow is reversed after each reading to reduce the impact of ion concentrations. The electrical-resistivity setup presently being constructed is similar to typical four-point measurements that are performed for geological applications (Chaker, 1996). The measured resistivities are more accurate than those determined with our initial across-the-test-specimen, two-point measurements which were used to map the location of gas hydrate within the test specimen (Booth et al., 1999).

3. PROCEDURES

3.1. Preservation of samples containing natural gas hydrate
We have recovered natural gas hydrate from two field projects: Ocean Drilling Program (ODP) Leg 164 conducted on the Blake Ridge off the coast of South Carolina (Paul et al., 1996) and the Mallik 21-38 Gas Hydrate Research Well drilled in the Northwest Territories of the Canadian Arctic (Dallimore et al., 1999). Although both projects had pressurized coring systems, gas-hydrate samples preserved for later laboratory testing were recovered using conventional drilling techniques. During the ODP cruise samples containing gas hydrate in finer-grained sediment were brought up through a relatively warm column of water above the thermocline before recovery.

This process contributed to gas hydrate decomposition. By contrast, the coarser-grained samples recovered in the Mackenzie Delta had to be brought up through 640 m of permafrost. The Mallik samples did freeze, but not because of the permafrost. Endothermic cooling produced by gas-hydrate dissociation caused the remaining free water to become ice. Samples from each area were placed into transportation pressure vessels, pressurized with gas, and stored within refrigerators or freezers to maintain the gas hydrate at stable pressure-temperature conditions for the overland trip to Woods Hole, MA.

3.2. Mallik 21-38 samples
The Mallik 21-38 test samples were kept frozen prior to placement in GHASTLI. They were removed from the transportation vessels, jacketed, and placed between end caps within a walk-in freezer maintained at about -30°C before being brought into the lab. The presence of ice helped to stabilize the hydrate at atmospheric pressure during the test setup procedures. Although the specimens were still partially frozen at the beginning of testing, they were allowed to warm to a temperature where the ice melted, but the gas hydrate remained solid.

Each GHASTLI laboratory test consists of different steps designed to address different physical-property measurements (Fig. 4). Initial acoustic measurements on gas hydrate and partially-ice-bonded samples (Fig. 5) were followed by converting the ice to water. Temperature was raised to approximately 4°C for at least 24 hours until all ice had melted and acoustic velocity stabilized. After all of the ice (which was not present in situ) melted, temperature was slowly raised in 1 to 2°C increments until dissociation began. The dissociated gas, specimen pore water, and water released from hydrate entered the back pressure collector where water and gas were separated and their volumes measured.

In all cases, the acoustic signal previously established was lost during initial dissociation of gas hydrate in the test samples but was recovered using a "rebuilding" procedure. One strength test was performed on a sample that contained gas hydrate; the rest were sheared after dissociation.
3.3. Laboratory-formed gas hydrate
GHASTLI has been used to form gas hydrate within a number of sediment types in the laboratory; for example, Ottawa sand (a standard sediment commonly used for testing), silt, and black sand (Figure 5). Gas hydrate can be formed a number of different ways using GHASTLI. In order to simulate in situ conditions, typically, a water-saturated sediment is initially brought to pressures between 12 and 20 MPa. Confining pressure is increased and consolidation is allowed until excess pore pressures are dissipated. The difference between the internal pore pressure and the confining pressure is related to the simulated overburden stress. Methane is percolated up through the sediment until a predetermined amount of water, measured by the collector, is pushed out of the sample. Then the temperature of the coolant flowing to the heat exchanger located above the top end cap is lowered until P-T conditions are within the gas-hydrate-stability zone. Physical properties are measured and recorded during these procedures. To dissociate the gas hydrate, the procedure is reversed; that is, the temperature is slowly raised until the phase boundary is crossed. Pressure, rather than temperature can also be used as the trigger to form or dissociate gas hydrate. Because the thermal gradient between the top and bottom of the sample can be adjusted from about one degree to many degrees, it is conceivable that a phase boundary can actually be induced at a layer in the sample.

4. RESULTS AND DISCUSSION - SELECTED EXAMPLES
4.1. Index properties and gas hydrate quantity
The index properties (e.g., water content, bulk density, void ratio, porosity) of reconstituted samples typically are calculated from the known mass of solids and water used to form the specimen. These calculations can then be checked with volumetric measurements. The reverse is true for "undisturbed" natural samples containing gas hydrate. Differences between porosity measurements can approximately be accounted for by the expansion of water to ice (about 9%) and water to gas hydrate (about 26%). The amount of methane present, in moles, is determined from the equation-of-state relationships presented by Duan et al. (1992).

4.2. Acoustic properties
P-wave signals are recorded at numerous times during testing (e.g., Fig. 4). P-wave velocities, \( V_p \), are calculated routinely also. Figure 6 shows velocity changes induced in different materials by gas hydrate formation, freezing of the pore water, and by increasing consolidation stress. Knowledge of the material occupying the pore space and the consolidation stress are critical to understanding the implications of the various velocity measurements. \( V_p \) values typically increase with consolidation stress because of the greater grain to grain contact stress (primarily) and increased density. This is illustrated by Figure 7 for a Mackenzie Delta sediment, but the rate of velocity change decreases with increasing pressure. Sample shortening during consolidation could also create an
apparent velocity increase due to reduced travel distance for the acoustic pulse (if sample height is not accurately measured). Initial results indicate that samples obtained from the Mackenzie Delta containing natural-gas hydrate acoustically behave as part of the sediment frame or as disseminated throughout the pore fluid, but not as cements between grains.

4.3. Strength properties of samples from Mallik 2L-38 Well
Preserving field samples that contain natural gas hydrate for subsequent laboratory strength testing is inherently difficult. Unless a pressurized coring system that can maintain in situ P-T conditions is used, some gas hydrate may be lost during sample transfer into transportation vessels in the field or later during transfer into a laboratory test system.

If gas hydrate behaves similarly to that of ice in sediment then gashydrate-bonded sediment should in most cases be stronger than similar material that does not contain gas hydrate. Andersland and Anderson (1978) demonstrate that the presence of ice can substantially increase the strength of sediment. Frozen sediment exhibits a wide range in strength properties, because strength is influenced by a number of factors: strain rate, temperature, confining pressure, grain size, and density. The strength of sediment containing gas hydrates is probably influenced by these and other factors such as gas hydrate-cage-occupancy.

![Diagram](image)

**Figure 6:** Comparison of changes in P-wave velocity for different materials tested in GHAHTLI by forming gas hydrate, freezing pore water, and increasing consolidation stress. The arrows represent an initial material velocity before the indicated process began, followed by a gradual increase in Vp until a final, maximum value is reached.

Undrained triaxial shear tests were performed on samples from the Mallik Well both before and after natural-gas hydrate was dissociated (Figure 8). Plots of the shear stress vs. axial strain for the four test samples show that the strength of the sample containing gas hydrate is indeed much higher. The gas-hydrate-containing sample exhibited higher negative pore pressures during shear. Andersland and Ladanyi (1994) indicate that frozen samples are typically plotted with respect to total stresses because of the difficulty in measuring intergranular stresses. Evidently, in the gas-hydrate-containing Mallik 2L-38 specimen, the pores contained enough free water to transmit pore pressure. The large difference in strength between the specimen containing gas hydrate and the other samples may be related to the fact that many of the pores of the gas-hydrate sample contained a solid that increased the tendency for dilation during shear. Hence the higher negative pore pressure and corresponding strength values.

The maximum effective friction angle (Holtz and Kovacs, 1981) for the hydrate sample was also the highest value of any of the tests (44.4°). The friction angles for the non-hydrate bearing samples (33.8 - 38.6°) are within the typical range of sandy sediment (Hunt, 1984). Depending upon the amount present, gas hydrate has the potential to greatly affect the mechanical properties of the host sediment.

The dissociation of methane hydrate in GHAHTLI produces an excess volume of gas which is related to the test pressure and temperature conditions. Typically during a test the internal sample pressure is maintained constant and the additional gas produced by dissociation is measured in the collector.
However, in situ, the production of excess gas may have a destabilizing effect because of the increase in pore pressure accompanied by a subsequent reduction in sediment effective stress. The amount of pressure generated in situ by dissociation depends upon a number of factors, some of which include: P-T conditions, amount and distribution of gas hydrate present, percent of cage occupancy of the hydrate by gas molecules, inherent sediment permeability, rate of dissociation, and faulting present in the region. Measuring sediment and gas hydrate properties is only the first step in predicting in situ behavior.

![Graph](image)

**Figure 8:** Comparison of triaxial strength plots for a sample containing natural gas hydrate to other samples from the Malilin 2L-38 well after gas hydrate was allowed to dissociate.

5. SUMMARY

GHASTLI is able to produce pressure and temperature conditions that simulate the natural environment. Gas hydrate can either be formed in: (1) undisturbed natural sediment, (2) reconstituted natural sediment, or (3) artificial material; and field samples containing natural-gas hydrate can be preserved. Physical properties, including acoustic velocity, shear strength, permeability, and electrical resistivity are measured at different times during testing to ascertain the effect that gas hydrate has on the bulk physical properties of the host sediment. Those physical properties are used in models that estimate the amount of gas hydrate present in situ, for seafloor and well stability calculations, and for comparison to well logs.

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Chapter 25

Laboratory synthesis of pure methane hydrate suitable for measurement of physical properties and decomposition behavior

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1. INTRODUCTION AND BACKGROUND

1.1. Why study synthetic gas hydrates?

Gas hydrates are an intriguing class of nonstoichiometric compounds that have significant commercial and scientific applications both as an energy resource and as a manufactured material. The last half-century has witnessed a marked escalation in the scope of experimental research on gas hydrates, particularly directed towards the determination of their phase equilibria, formation kinetics, crystallographic and structural properties, transport and thermal properties, effects of inhibitors, and a number of related geochemical topics.

There remains, however, a paucity of reliable experimental measurements of many of the physical, material, thermal, acoustic, and elastic properties of most pure, end-member hydrocarbon hydrates. Instead, either water ice, or hydrates readily formed in the laboratory but rarely occurring in nature (such as ethylene-oxide hydrate and THF hydrate), have commonly been used as analogue material for property measurements. Consequently, there does not exist an accurate and comprehensive database of physical and material properties for end-member gas hydrates, and particularly for those hydrates that are more problematic to form and stabilize in the laboratory. Compounding this problem is the difficulty in retrieving pristine material from natural settings on which to make such measurements, in different laboratories using different methods, and in the general lack of agreement of measurements made on synthetic material.

A wide variety of processes and techniques have been used to synthesize gas hydrates in the laboratory, each yielding a final product that may be highly suitable for some types of experimental testing while clearly unsuitable for others. Here, we focus on laboratory production of pure, polycrystalline methane hydrate and hydrate-sediment aggregates that are suitable for a variety of physical and material properties measurements made on pure, end-member