

## ULTRASONIC VELOCITIES IN LABORATORY-FORMED GAS HYDRATE-BEARING SEDIMENTS

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### Abstract

Gas Hydrates are widely distributed in the near surface at high latitudes and many ocean bottoms. Our laboratory measurements help calibrate the seismic and well log data that are used to ascertain the in situ distribution of hydrates. Ultrasonic velocities are measured in unconsolidated sand specimen under thermobaric conditions comparable to those found in shallow oceanic or permafrost regions, i.e. in the gas hydrate stability zone. Compressional-wave (p-wave) velocity data in *dry* Ottawa Sand samples subjected to a confining pressure that from 2 to 20 MPa range from about 700 to 1500 m/s. Gas hydrates were then formed a partially saturated Ottawa sand sample. As expected, this hydrate formation resulted in a dramatic increase in p-wave velocities from 700 m/s in the partially water saturated sample to 2100 m/s in the hydrate-bearing specimen. The hydrate effectively cements the sand such that nine hours after entering the hydrate stability region, the recorded waveforms remained constant even as the confining pressure was increased by more than 10 MPa.

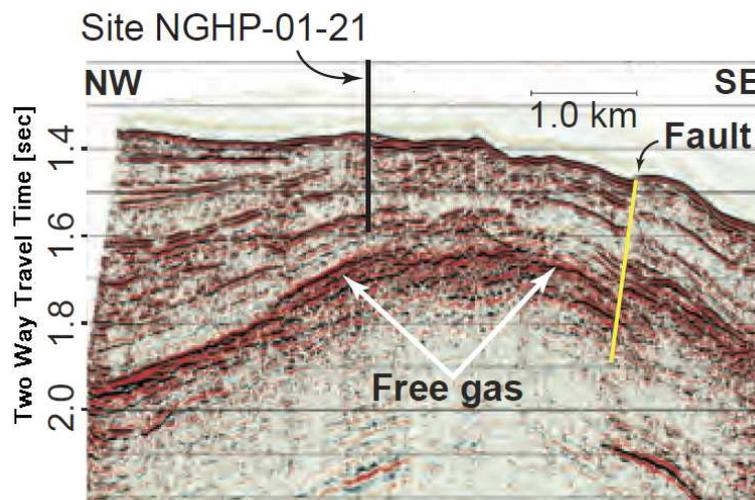
### Introduction

Gas hydrates are crystalline structures where a framework or 'cage' of water contains a guest molecule. In most natural hydrates, methane is contained within the water frame. These materials form and are stable under low temperatures and elevated pressures. The occurrence of natural hydrates is wide spread in arctic regions and in deep water sediments. Interest in hydrates is becoming more intense and they are perceived as a resource; a geohazard; and potential contributor to climate change. Estimates suggest that as a resource, the gas contained in natural hydrates match surpass that in conventional reservoirs. On the other hand, the occurrence of hydrates at or near the ocean floor can destabilize structures such as production platforms. In addition, another concern is that if widespread destabilization of hydrates occurs, substantial amounts of methane will be released, contributing to climate change.

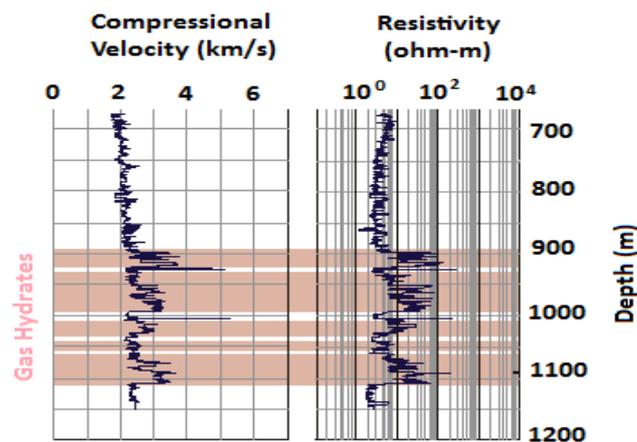
The distribution and quantity of hydrates in place is usually made by a combination of seismic, well log information. However, estimates of the total available hydrates vary enormously depending on how one interprets the hydrate signature in seismic data. For example, Figure 1 shows a seismic section complicated by the presence of both hydrates and free gas. Well logs (Figure 2) pose a similar problem, since the measured response depends on the location and fabric of the hydrate within the sediment. As a result, laboratory measurements are required to calibrate the remote geophysical measurements. Natural gas hydrate-cores are rare, costly, heterogeneous, and almost always show some degree of damage. As an alternative, sediments containing laboratory-formed gas hydrates are often used to provide calibration data for well-logs and seismic. There are a number of different ways to form gas hydrate in sediment, and each

laboratory generally has its preferred technique. (Hyndman & Dallimore, 2001). Gas Hydrate occurrences are indicated by an increase in both sonic velocity and resistivity.

Previous work has shown that the method of hydrate formation tends to control the hydrate distribution within the sample, which impacts the physical properties of the sample. To date, however, no comprehensive testing has been conducted within a single experimental apparatus that would allow a quantitative comparison between the different hydrate formation techniques, and show the differences in the resulting hydrate distributions, as well as how those differences manifest themselves as bulk physical properties. The objective of this project was to construct an apparatus that allows us to investigate the effect on gas hydrate formation method on ultrasonic velocities.



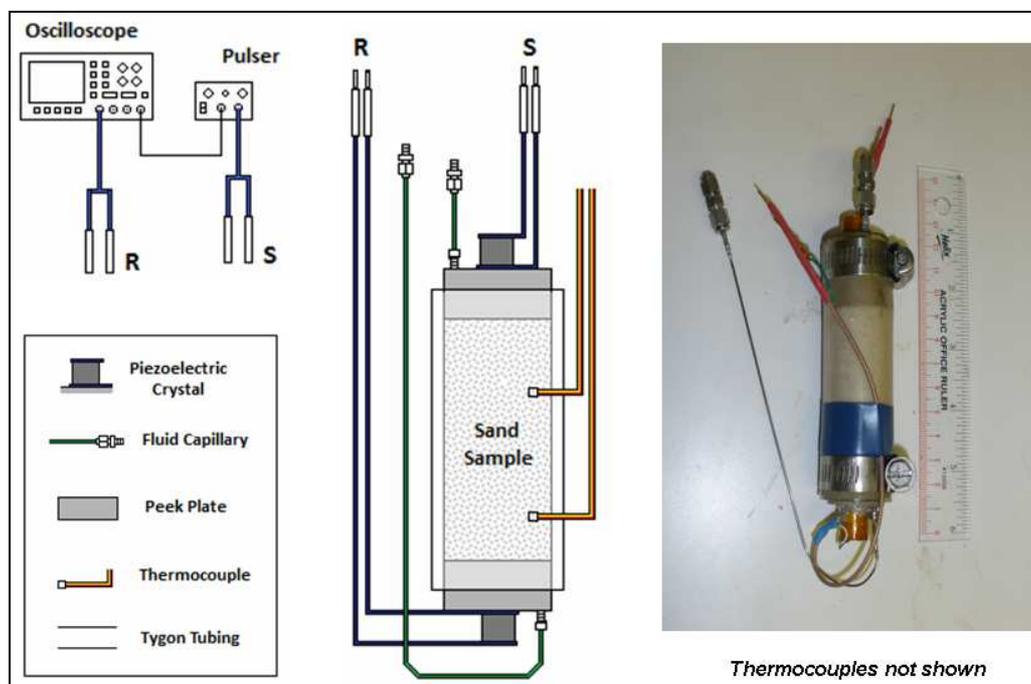
**Figure 1:** Seismic line crossing drill Site NGHP-01- 21 (Collett *et al.*, 2008). The reflection is complicated due both to the potential presence of hydrate as well as free gas.



**Figure 2:** Sonic and Resistivity Log recorded at the JPEX/JNOC/GNC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada (Modified after Hyndman & Dallimore, 2001).

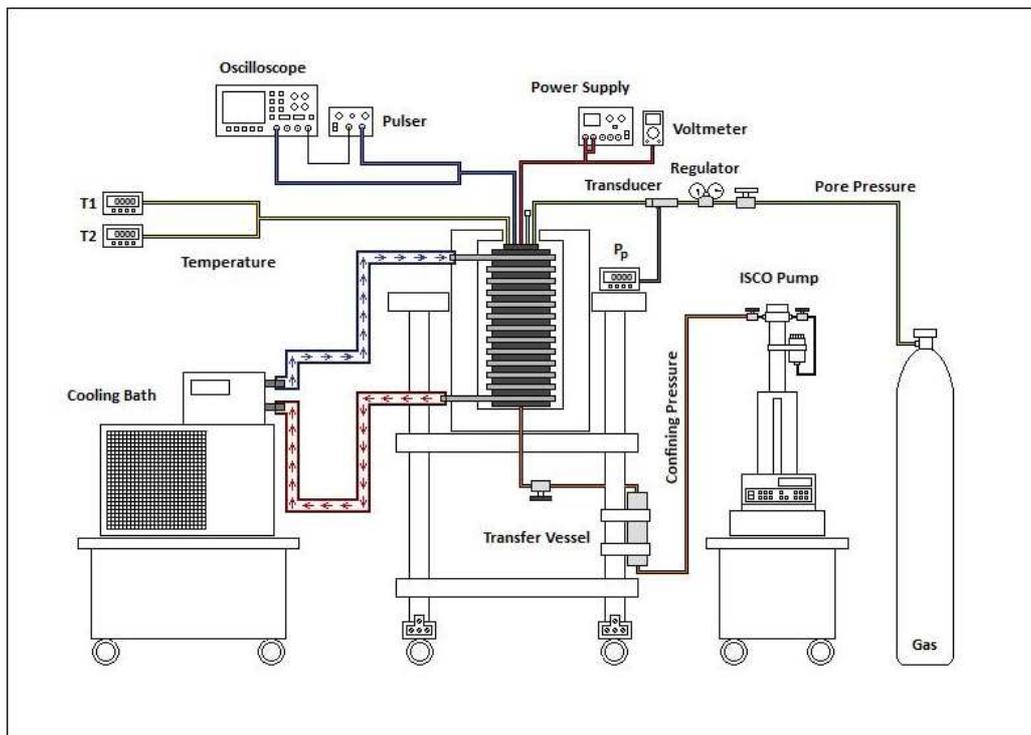
## Experimental Configuration

We designed and built an experimental setup that would allow us to measure p-wave velocities in sediments during gas hydrate formation and dissociation under in situ conditions. The setup consists of a temperature-controlled pressure vessel filled with hydraulic oil which confines an instrumented sample holder. A maximum pressure of 20 MPa can be applied to the sample at temperatures between 25°C and -5°C. As can be seen in Figure 3, the sample is sandwiched between a pair of cylindrical end caps and is jacketed with flexible Tygon tubing. Ultrasonic transducers made of 100 kHz piezoelectric crystals are mounted on top of the end caps to generate and record the compression wave signal. The end caps have a diameter of  $(25.40 \pm 0.02)$  mm and are made of polyaryletheretherketone (PEEK). Often, metal end caps are used to hold the ultrasonic transducers. However, Zimmer et al. (2007) showed that the use of plastic transducer plates improves the impedance matching between transducer and sample when unconsolidated sand samples are measured. A high voltage pulse is utilized to excite one transducer and the velocity of the transmitted pulse is calculated by picking first arrivals from the recorded waveforms that are displayed on the oscilloscope. Both end caps also contain ports that enable fluid circulation through the sample and pore-pressure control. The end caps and sand sample are incased in a flexible jacket to isolate the sample from the confining fluid. Thermocouples are placed outside the sample holder to monitor the sample temperature with an accuracy of  $\pm 0.5^\circ\text{C}$ . Furthermore, linear potentiometers are attached to top and bottom end caps to measure changes in length ( $\pm 0.2$  mm) when the sample is subjected to pore and confining pressure. Pressure is controlled by an external ISCO pump with an accuracy of  $\pm 1.5\%$ .



**Figure 3:** Instrumented Sample Holder Setup

In the current configuration (Figure 4), methane is injected into the sand sample to provide the desired pore pressure. Methane flow is controlled through a gas regulator and is monitored using a pressure transducer with an error of  $\pm 0.2\%$ . The insulated vessel is cooled by circulating ethylene glycol from a cooling bath. Sample temperatures and pore pressures are digitized and stored in a computer as a function of time.



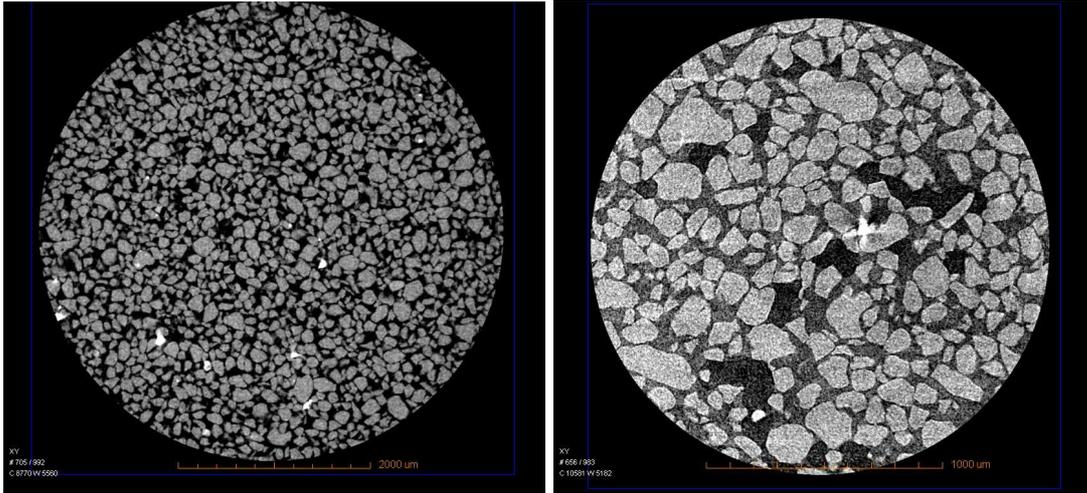
**Figure 4:** Experimental Setup for Ultrasonic Velocity Measurements on gas hydrate-bearing sediments.

## Sample Preparation and Measurements

### *Dry Ottawa Sand*

In an attempt to make measurements from different research facilities comparable, hydrate-researching institutes such as the USGS in Woods Hole, LBNL, GeorgiaTech as well as the CSM Center for Rock Abuse agreed on exclusively using Ottawa Sand Type F110 when forming gas hydrate-bearing specimen in the laboratory. This type of Ottawa Sand is mainly composed of quartz (>99%) and has a density of  $2650 \text{ kg/m}^3$ . Figure 5 shows micro-X-Ray CT images obtained of dry and partially water-saturated Ottawa Sand F110. Each prepared sand specimen sample is approximately  $(25.40 \pm 0.02)$  mm in diameter, but have variable length. The length of each specimen was measured with a digital caliper and is given in Table 1. An amount of Ottawa sand was filled into the sample holder, and compacted by hand using a Teflon tamping stick. The porosity of each specimen was calculated from dimensions of each sample, its mass and

the sand density. The prepared samples were placed inside the pressure vessel and subjected to the respective confining pressure while the pore pressure remained at atmospheric conditions. Sample 1 was tested under increasing confining pressure at 1, 2, 3, 4, 5, 10, 15, and 20 MPa, whereas Sample 2 and 4 were first subjected to an initial confining pressure of 20 MPa, which was then decreased incrementally.



**Figure 5:** a) dry and b) partially water saturated Ottawa Sand (Micro X-Ray CT)

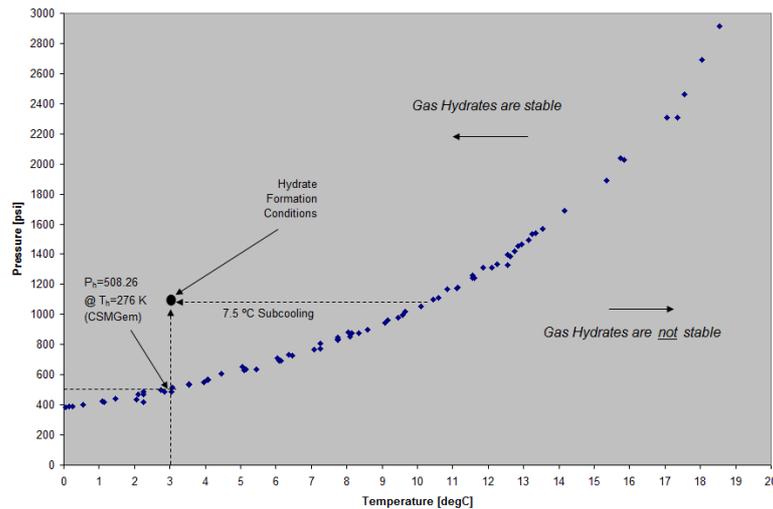
**Table 1:** Properties of Sample Preparation and Specimen

Sample	Length (mm)	Mass (g)	$\phi_{\text{initial}}$	Layers	Compaction
SMPL_1	69.6± 0.23	54.0± 0.1	0.42	8	60±1 s/layer
SMPL_2	36.3± 0.64	30.0± 0.1	0.39	10	90±1 s/layer
SMPL_4	37.2± 0.27	30.0± 0.1	0.40	10	90±1 s/layer

### ***Methane-Hydrate-Bearing Ottawa Sand***

To prepare the partially water-saturated sand sample, 93 wt% Ottawa Sand F110 and 7 wt% distilled water were mixed thoroughly in a plastic bag. The total mass of the sample and its length were measured as (35.74±0.10) g and (42.60±0.08) mm, respectively, which results in an initial porosity of 42% and an initial water saturation (fraction of pore space occupied with water) of about 27.5 %. After the sample assembly was placed inside the pressure vessel, the temperature of the system is lowered employing the external cooling system. It takes about 48 hours to cool the heavy, oil-filled steel vessel down to the designated temperatures of about 2.5- 3.0 °C. After the temperature stabilized, a confining pressure of 3 MPa was applied to the sample. Afterward the methane was injected into the sample and the pore pressure is raised to 1 MPa below the confining pressure. Then, both confining and pore pressure were increased by 1 MPa and held constant for about an hour to allow injection of methane

gas. The pore pressure at that point was just below the methane hydrate equilibrium pressure, which at 2.5 °C has a value of about 3.3 MPa (Figure 6). Once the sample temperature returned to its designated value, confining and pore pressure are further increased to 10 MPa and 7.5 MPa, respectively, and held constant. Ultrasonic waveforms are recorded every hour until the no more obvious changes in the waveforms occur. The confining pressure is then increased to about 20 MPa, after that incrementally decreased, and waveforms are recorded after every increment of 1 MPa.



**Figure 6:** Phase diagram for methane hydrate (modified after Sloan & Koh, 2008)

## Results

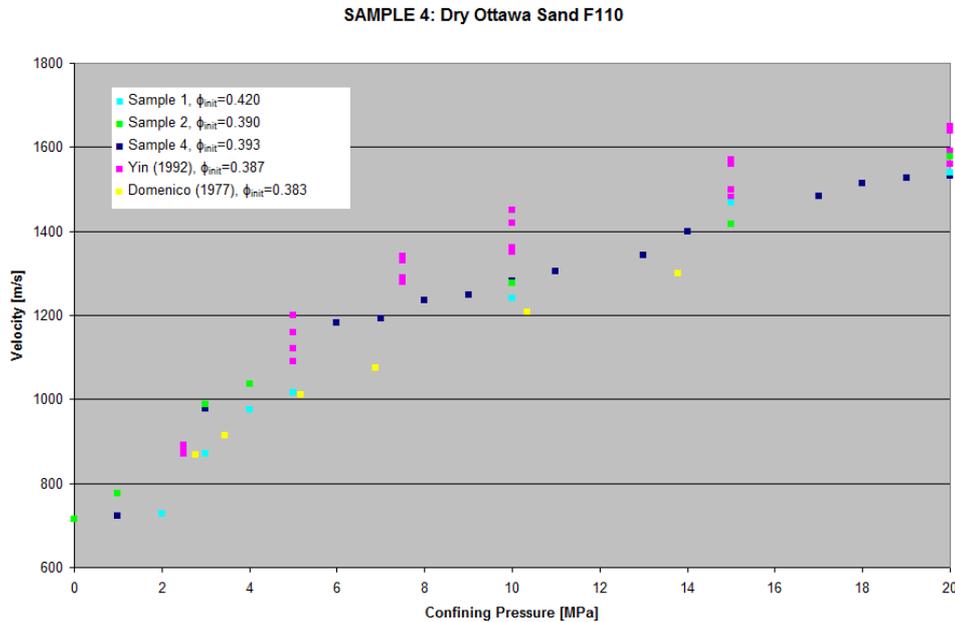
### *Dry Ottawa Sand*

Figure 7 shows typical waveforms obtained for the dry Ottawa Sand samples measured under confining pressure. The p-wave velocities were calculated by picking first arrivals from the recorded pulse-transmission signals and are listed in Table 2. Figure 8 shows our measured p-wave velocities as a function of confining pressure alongside literature values. All data points depicted were collected for Ottawa Sand samples of similar initial porosities. Differences are small, and the variations among the results may be attributed to differences in sediment properties (grain size distribution, composition) or experimental settings (measurement frequency, etc.).

### *Methane-Hydrate-Bearing Ottawa Sand*

Methane development is time-dependent, and waveforms change as a function of time. After about 25 minutes after the gas hydrate stability curve was surpassed noticeable changes occur in the waveform. Formation of hydrate results in a decrease in traveltime (increase in velocity) that is quite significant. Figure 9 shows the p-wave velocity increase with time and, most probably, with increasing gas hydrate saturation. The hydrate growth appears to stop after about 9 hours, which might indicate that either all the water was converted into hydrate or that the hydrate growth blocked all the pores near the gas inlet making the sample impermeable and, thus, preventing further hydrate



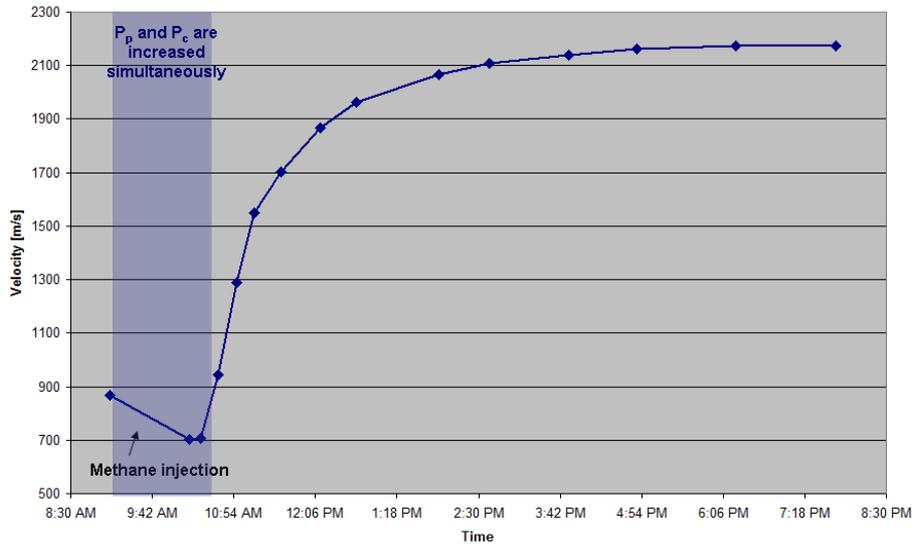


**Figure 8:** P-wave velocity in Ottawa sand versus confining pressure

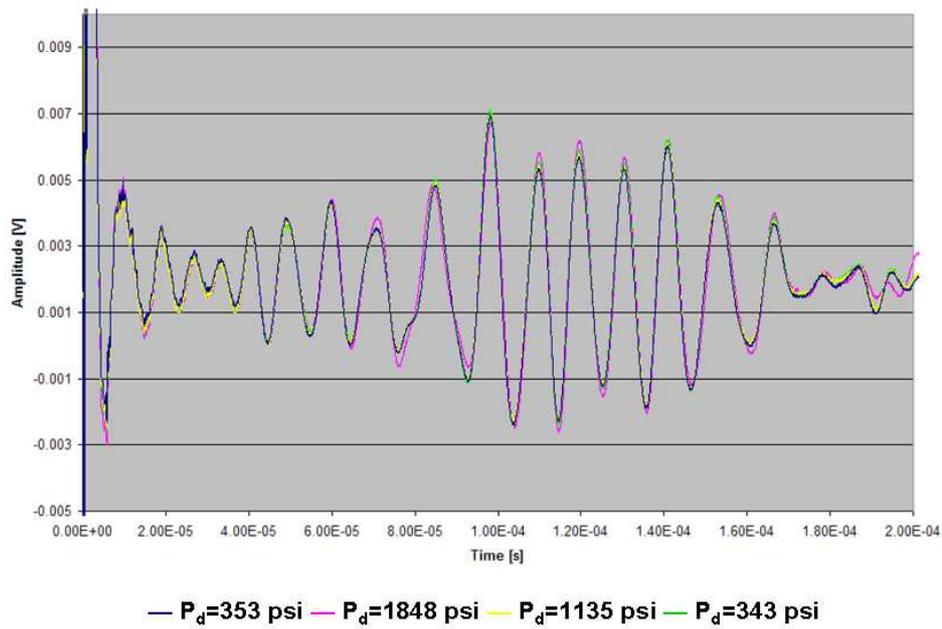
This indicates that the sample might entirely be cemented with methane hydrate and can not undergo any further change in length under the confining pressures applied. After the measurements were completed, the sample was quickly recovered from the pressure vessel and sample holder. Because of the fine grain size gas hydrates could not be observed visually, but audible fizzing indicated the presence of dissociating gas hydrate in the sediment. Also, when part of the sand was submersed into water, gas bubbles emerged from the sand, which collapsed soon after as the hydrate fully decomposed.

## Conclusions

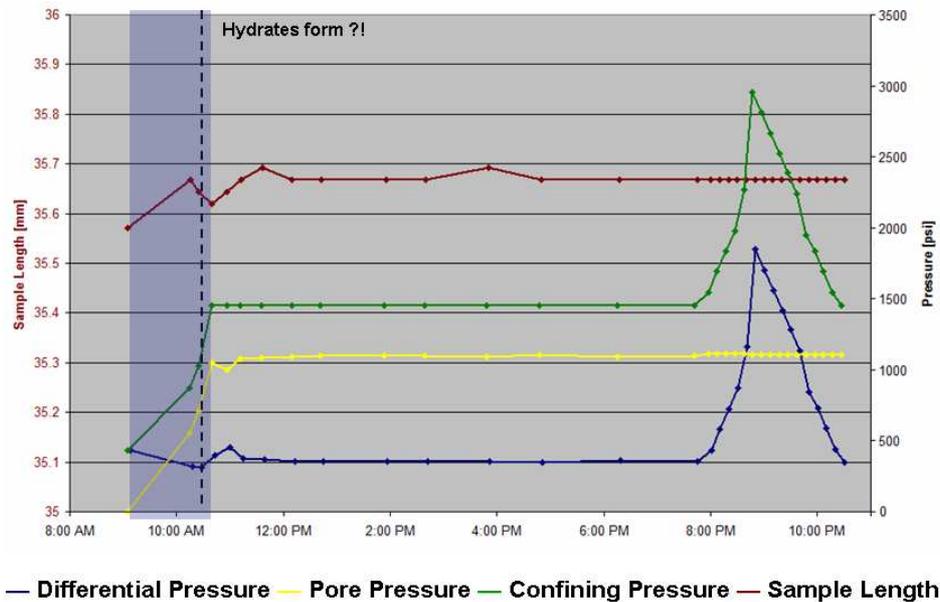
Ultrasonic velocity measurements were performed on dry and hydrate-bearing sand using our newly constructed experimental setup. The results obtained for the dry Ottawa sand samples agree with data found in literature. Methane hydrate-bearing sediment was successfully generated by pressurizing partially water-saturated Ottawa sand. The data collected during the hydrate-formation process exhibits a logarithmic increase in p-wave velocity with time. Approximately nine hours after an increase in velocity was first observed, the waveforms remained unchanged indicating that hydrate formation stopped. Whether this behavior is due to full hydrate conversion or hydrate blocking gas pathways within the sand can not be answered with certainty. Planned Micro-CT measurements will help to interpret how gas hydrate content and distribution relate to p-wave velocities. In the next phase of the project, further ultrasonic compressional- and shear-wave measurement on gas hydrate-bearing sediments will be made. We will measure a series of hydrated Ottawa sand samples that will be formed using different hydrate formation techniques, e.g. bubbling gas through fully water-saturated samples, using tetrahydrofuran (THF).



**Figure 9:** Gas hydrate formation: p-wave velocities versus time



**Figure 10:** Pressure independence of p-wave velocities in hydrate-cemented sand



**Figure 11:** Sample length and pressures during the duration of the experiment

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