FINAL REPORT

CHARACTERIZATION OF NATURAL GAS HYDRATES RESEARCH

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(TASK 3)

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Summary

Current research and development at Gas Technology Institute is focused on characterization of natural gas hydrates as an energy resource. The fundamental research objective is to develop a fundamental understanding of hydrate-bearing sediments as reservoir rocks. Specifically, the work is aimed at development of data and information required for prediction of hydrates' dissociation rate as a function of the host rock properties such as porosity and permeability and translation of the data to prediction of production rate and ultimate recovery from hydrate saturated sediments.

To achieve the stated objective, a dedicated experiment station capable of creation and controlled dissociation of hydrate-bearing specimens and continuous monitoring of the processes was designed, manufactured and assembled. The present paper describes the interim results from these experiments.

Results to date, as presented in this paper, prove that it is indeed possible to monitor the dissociation process through ultrasonic pseudo-tomographic imaging and it is possible to develop a catalog of data relating the dissociation rates to host rock properties for a variety of sedimentary rocks. This data can be used for calibration of numerical data and provision of input parameters for flow prediction at reservoir scale. The data presented in this paper are intended to provide the proof of concept. As the work continues the intended comprehensive data set will be completed and published.

Introduction

Natural gas hydrates are ice-like substances that form through entrapment of hydrocarbon molecules inside the lattice of ice crystals. Figure 1 is a schematic representation of a methane hydrate crystal. Hydrate crystals are formed under certain pressure and temperature conditions where the temperature may be above the melting temperature for ice. For example, at pressures above 2000 psi a methane hydrate crystal would be stable at 60° F (Fig. 2). The gas content of a hydrate crystal can be as much as 170 times the volume of the crystal; i.e., one cubic foot of methane hydrate can contain up to 170 standard cubic feet of methane.

Figure 1. Schematic representation of a methane hydrate crystal.

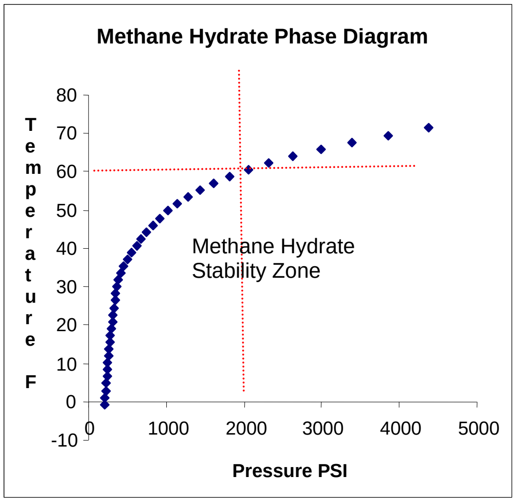


Figure 2. Methane hydrate phase diagram.

From a gas industry perspective, gas hydrates are both a nuisance and a blessing. They are a nuisance as they plug the pipes and valves and interrupt the flow of gas and they are a blessing because naturally occurring gas hydrates constitute an immense natural gas resource. Because gas hydrates are stable at temperatures above the freezing temperature of ice, their occurrence is not limited to cold regions of the earth. Gas hydrates are present as mounds on deeper sea floor, in hydrate-bearing sediments beneath the sea floor, as well as hydrate zones below permafrost in the arctic region. The latest worldwide estimate of natural gas entrapped in hydrates is at 700,000 trillion cubic feet (TCF). The worldwide distribution of natural gas hydrates is shown on Figure 3.

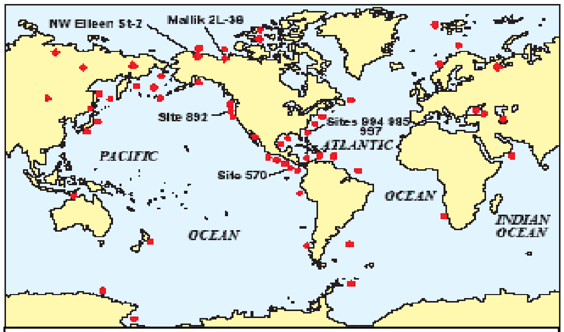


Figure 3. Worldwide distribution of natural gas hydrates

The presence of natural gas hydrates has been established by direct observations through various sea floor expeditions, numerous ocean drilling and coring projects, drilling in the arctic region; and indirect detection from seismic data. In the latter case, the sharp acoustic impedance contrast between hydrate zones and the underlying free gas zone gives rise to very strong reflection events that remain consistent across the hydrate accumulation. The lower depth limit of hydrate stability zone occurs where geothermal gradient intersects the hydrate stability curve; i.e., where the earth temperature is above equilibrium temperature for the pressure at that depth. As a result, the interface between hydrate zone and free gas zones parallels the sea floor and the corresponding reflection events have been known as the Bottom Simulating Reflections (BSR). An example of a strong BSR can be readily identified on figure 4. The seismic cross section on this figure is from the survey over the crest of Blake Ridge, offshore South Carolina.

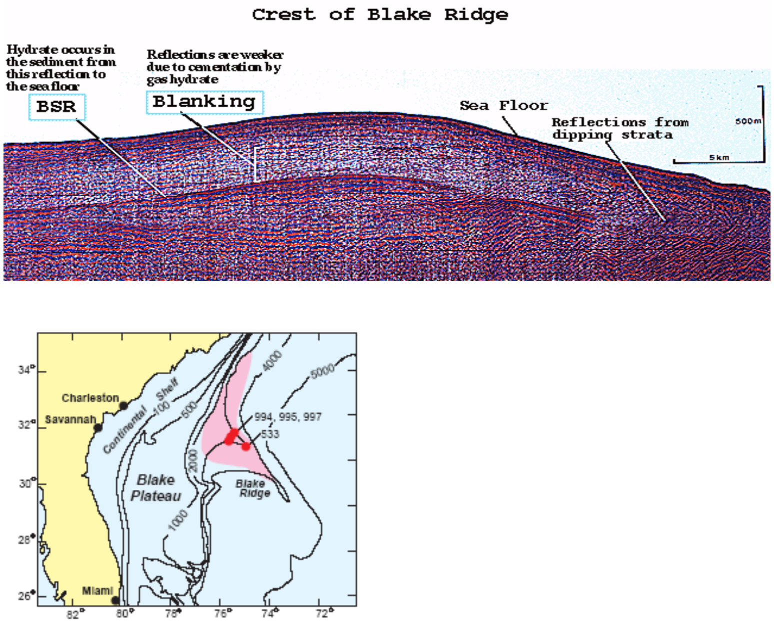
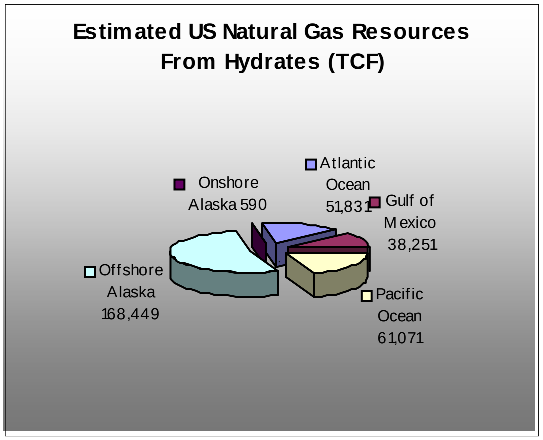


Figure 4. Seismic cross section across Blake Ridge, offshore South Carolina.

In the United States, the mean estimate of the volume of natural gas entrapped in hydrates is 320,000 TCF (Table 1). This estimate has been recently revised to 200,000 TCF. This immense volume of potential reserve has revived the interest in this area. In fact, if as little as one percent of this resource could be turned to producible reserve, it would be enough to provide the entire United States natural gas demand for many decades.

Table 1. Mean estimate of major methane hydrate accumulations in the United States

Region	Volume (TCF)
Atlantic Ocean	51,831
Gulf of Mexico	38,251
Offshore Alaska	168,449
Onshore Alaska	590
Pacific Ocean	61,071
Total	320,192



Note. *This estimate has been recently revised to 200,000 TCF.*

Recent research efforts on gas hydrates have been focused on three areas:

- Inhibition of hydrate formation in wellheads and pipelines,
- Identification and delineation of hydrate accumulations at or below sea floor, and
- Development of exploration and production techniques for production from natural gas hydrates.

It can be safely stated that thermodynamics of hydrates has been well understood and chemical inhibitors and their methods of application have been developed. At the present time, nearly all major research and development activities are focused on the second and third issues mentioned above. Currently, scores of worldwide research and development projects are underway a good number of which are focused on characterization of naturally occurring hydrates as a resource. In the United States alone, the Department of Energy is supporting upward of twenty small and large projects. These projects include:

- Chevron-Texaco Gulf of Mexico project: Characterization of naturally occurring hydrates in deep Gulf of Mexico. Participants: US Depertment of Energy, US Department of Interior, Chevron-Texaco, Schlumberger, Halliburton, ConocoPhillips, TotalFinaElf, Japan National Oil Corp.
- BP Exploration project: Determination of commercial viability of production from hydrates.
- Maurer-Anadarko project: Development of technology to drill and produce from gas hydrates.
- Mallik project, Mackenzie Delta, Canada: International consortium aimed at development of production from hydrates. Participants: USA, Canada, Japan, Germany, India, International Continental Scientific Drilling Program
- GTI projects: 2 project
- National Laboratories; 13 projects.
- USGS: 3 major projects and active participation in nearly all hydrate-related research and development projects.
- Universities: 5 projects

In addition, Japan is pursing intensive research and development work aimed at establishing commercial production from the Nankai through. Many European countries, Russia, India, China, and many others are actively engaged in various research and development projects focused on production from hydrates.

Summary of GTI Research and Development Project

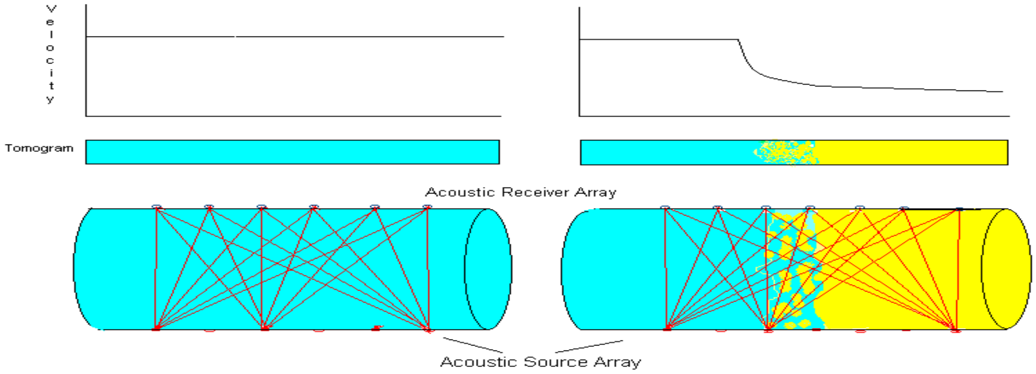
Research on natural gas hydrates at GTI is focused on characterization of hydrate-bearing sediments as a reservoir rock. To understand any aspect of the methane hydrates resource, be it safety issues or the exploitation methodology, the dissociation mode and rate as well as the resulting deformation of the host rocks must be understood and predictable. In so far as the production from hydrates is concerned, economics of any candidate project hinges on the production rate and the ultimate recovery both of which vary as a function the dissociation rate and are dependent of the behavior of the reservoir unit as a "whole". At this point in time, neither the flow mechanisms within hydrate reservoirs, nor dynamic changes that may result from the dissociation process are clearly understood. In fact, it is quite likely that severe deformations and seafloor instability that may be caused by dissociation of hydrates in rocks that form ideal reservoirs for conventional hydrocarbon production (e.g., 25% porosity coarse grain unconsolidated sands) could be such that production from these formations would be unsafe and impractical. It is therefore conceivable that competent rocks with low to moderate porosity and permeability may constitute the only reservoir condition amenable to production of the entrapped gas. However, characteristics of dissociation process and flow mechanism in these formations are at this time unknown. Realizing that the dissociation rate as a function of pressure decrease, or temperature increase, is the key factor controlling production from these formations, determination of the dissociation mode and rate within the host formation is a crucial imperative for identification of promising host formations and projection of expected production from these formations.

The primary focus of GTI project has been on laboratory measurements of dissociation of hydrates residing in a variety of rocks with different porosity and permeability and hydrate saturation. Laboratory measurements were performed on a number of man-made samples resembling the actual reservoir rocks. In these tests, the mode and expansion rate of the dissociated methane as a function of pressure/temperature changes were measured and recorded. The ultimate objective has been to develop a family dissociation data, or type curves, for a variety of reservoir rocks at the typical porosity and permeability ranges.

The overall scheme of laboratory measurements was to measure and monitor changes in elastic properties of hydrate bearing sediments during the dissociation process. Experiment setups were based on the premise that once hydrate dissociation would take place and a gas phase would evolve in the pore space, the bulk acoustic velocity of the specimen would be reduced significantly (See figure 5, top). As such, continuous velocity measurements along the sample during the process would in essence provide an image of the dissociation front at any point in time. Concurrent measurement of pressure and temperature would complement the information for a complete understanding of the process. Thus, maintaining a constant pressure/temperature condition for samples with different porosity, permeability, and saturation would provide the fundamental data for characterization of dissociation rate for various hydrate reservoir conditions.

A specialized experiment station for performing these measurements was designed, manufactured, and assembled. The setup included a 16 by 2.75 inch elastic cylindrical instrumented sleeve housing two diagonal arrays of acoustic source/receiver transducers. Figure 5 is a schematic diagram depicting the concept and figure 6 is the actual design diagram for the complete system. Figure 6 is the image of actual instrumented sleeve.

The instrumented sleeve is housed in a high pressure cell (Figure 7) with 5000 psi working pressure and equipped with various electrical feed-through and manifold for controlling flow through the sleeve and the confining space (Figures 8 and 9). During the experiment, the assembled unit is placed in the temperature-controlled chamber with a working temperature range of -60° to +375° F. Figure 9 is the picture of the fully assem



Tomographic Imaging of Hydrates Disassociation Front

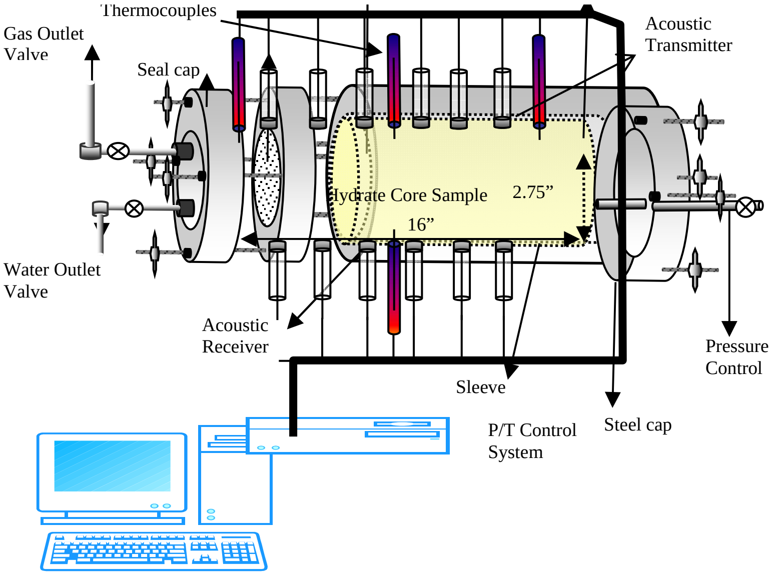
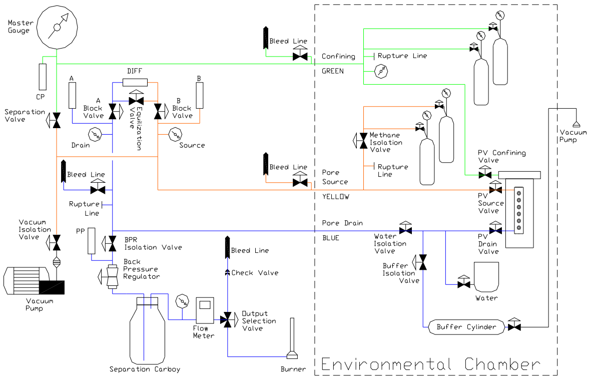


Figure 5. Schematic diagram of hydrates experiment station.



Hydrates Resource Characterization Laboratory
Synthesis Aperatus - Gas Line Diagram

All lines are 1/4" stainless steel tubing or flex hose rated at 4500 psi min.
Bleed Lines are 3/16" ID rubber hose rated at 250 psi with a check valve protecting the carboy.
Rupture Lines are 1/2" stainless steel tubing rated at 4500 psi min. with check valve protecting the bleed lines.

Figure 6. Design diagram for hydrates experiment station.

Figure 7. Instrumented sleeve held above reaction cell.

Figure 8. Assembled reaction cell inside temperature controlled chamber.

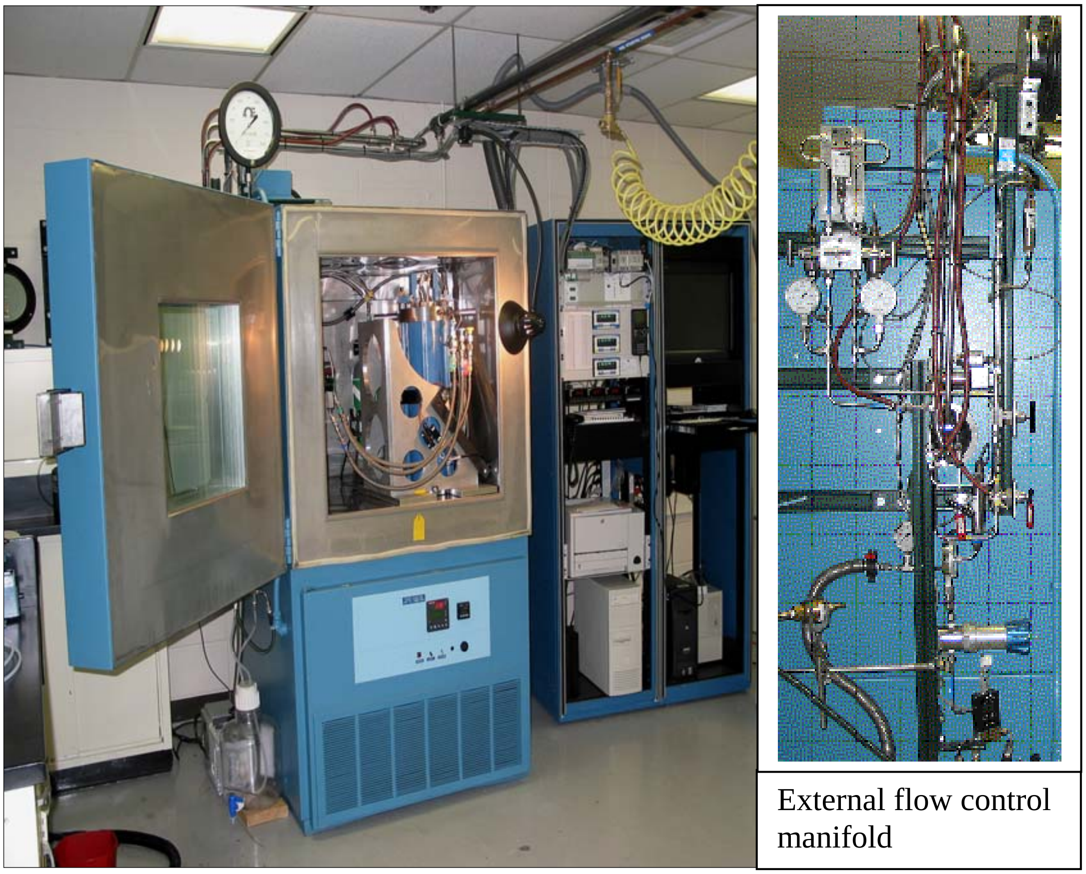


Figure 9. Hydrates Resource Characterization Experiment Station.

Procedure

The first step in our experiments are to create synthetic hydrate bearing sediments. The basic hydrate synthesis approach proposed by Sloan and others are followed by preparing sand/ice mixtures at freezing temperature, placing the mixture inside the instrumented sleeve, placing the sleeve inside the reaction cell, connecting the chilled methane source, and setting the pressure/temperature control at the desired level. The synthesis begins by slowly warming up the system to several degrees above freezing temperature under certain pressure (10-20MPa), and then cooling down to –10°C. This process (annealing) is repeated two to four for 2-4 times or until no more sign of reaction would be observed. For loose sand pack sediments, 60/80 meshes and for natural sandstone Yellow Berea are used. The example shown on Figure 10 exhibits changes in compressional wave travel time during the repeated annealing process in an initially water saturated sand pack. Referring to figure 10, it is clear that at the end of the 6th cycle although the temperature is well above melting temperature of ice, the travel time corresponds to that of hydrate-cemented sand.

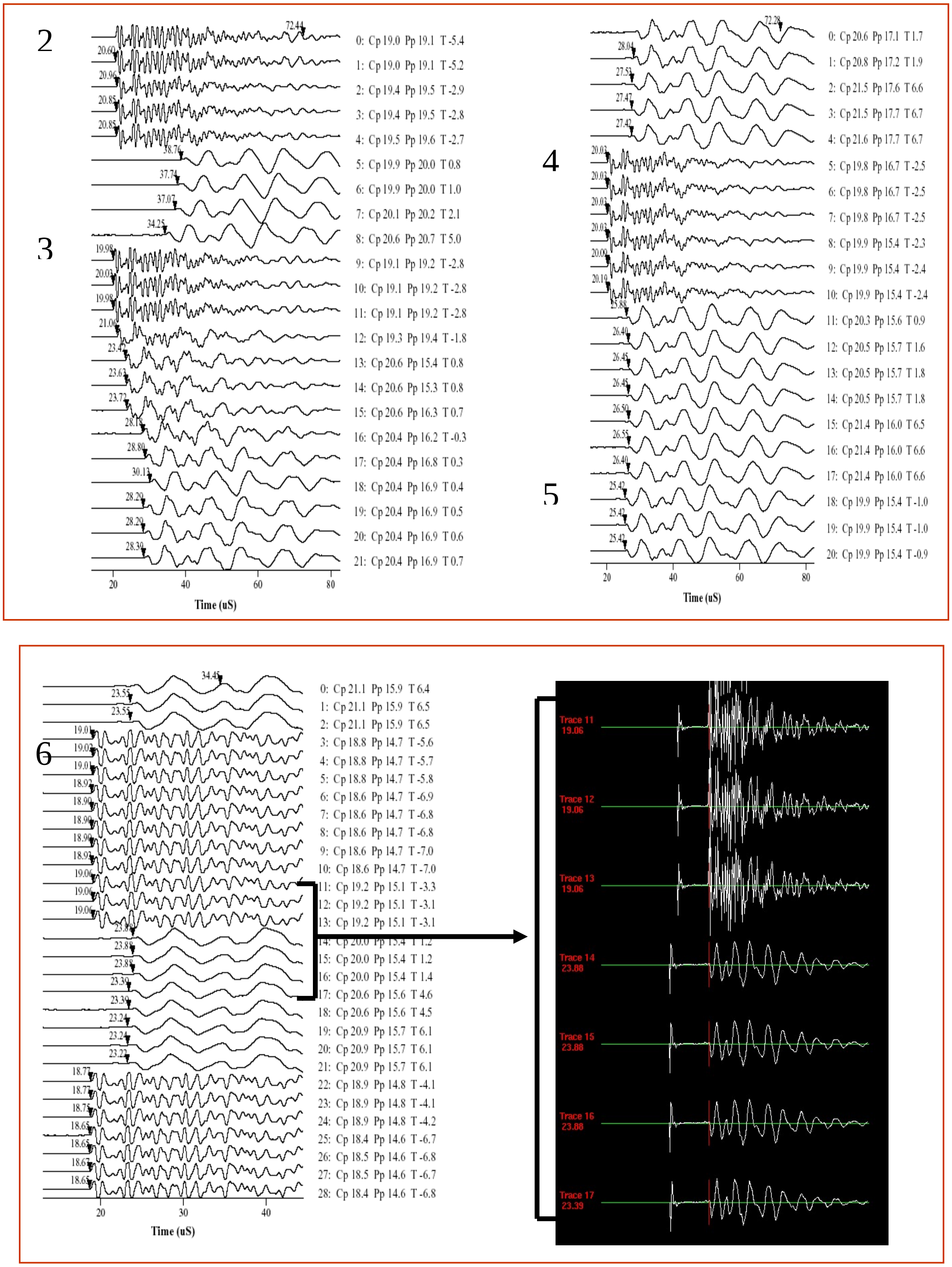


Figure 10. Observation of P-wave arrival time change during the synthesis cycles for 60/80 loose sand pack, 35% porosity, 76% initial water saturation.

After completion of the synthesis stage, the dissociation process is initiated by reducing the pore pressure (pressure inside the sleeve) or turning on the heat source at one end of the instrumented sleeve while marinating the confining and pore pressures constant. Figures 11 a through d show continuous travel time measurement during the dissociation process.

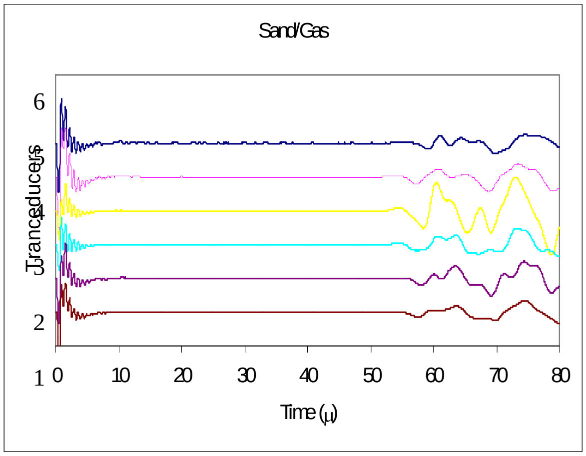


Figure 11-a. Travel time for sand/ice.

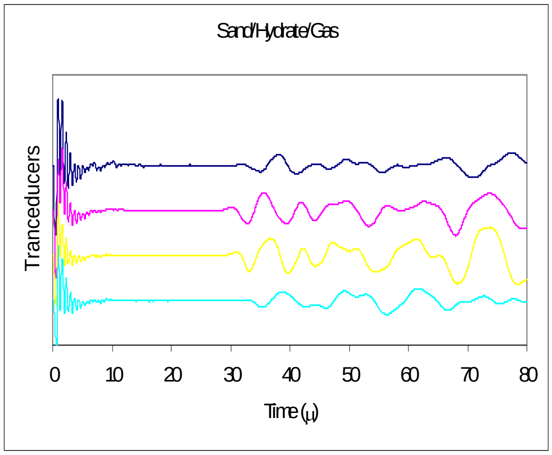


Figure 11-b. Travel time for hydrate/sand.

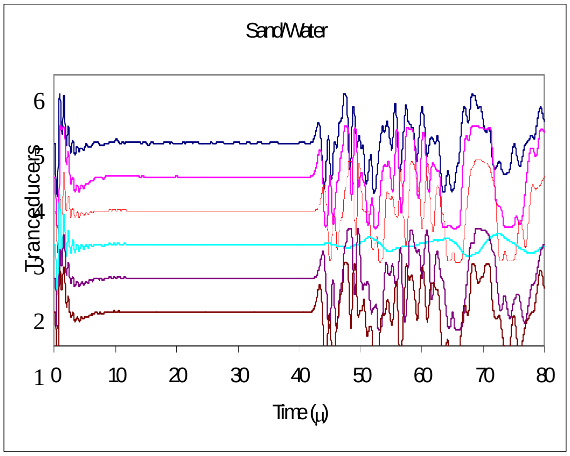


Figure 11-c. Travel time for water/sand.

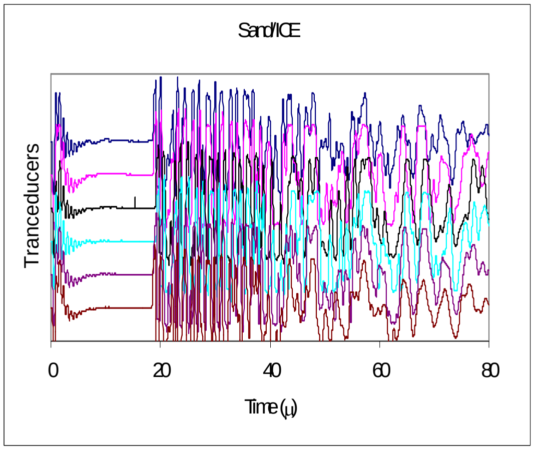


Figure 11-d. Travel time for sand/ice.

We noticed through several experiments that dissociation through depressurization was slow and intermittent, perhaps because of formation of ice and/or hydrate within the sample and in the flow line. Subsequently, a small 7-Watt heating element was placed at one end of the instrumented sleeve and was used to induce the dissociation process. A backpressure controller valve maintained constant pore pressure during the process. Figure 12 is a collage of the data from one source/receiver transducer pairs located five inches away from the heat source. Note a small and gradual increase in travel time before the dissociation front reaches the transducer pair (Arrow A, fast travel time). This is interpreted as being due to backflow of gas into the system. Arrow B (blank time zone) corresponds to the interval when actual dissociation takes place in the space occupied between the sensor pairs. This interval is indicative of sleeve deformation causing tilting of the source and receiver mounts and hampering the direct arrival of the transmitted energy. Finally, after the dissociation front passes the sensor pair, sleeve returns to its original shape (Arrow C, slow travel time).

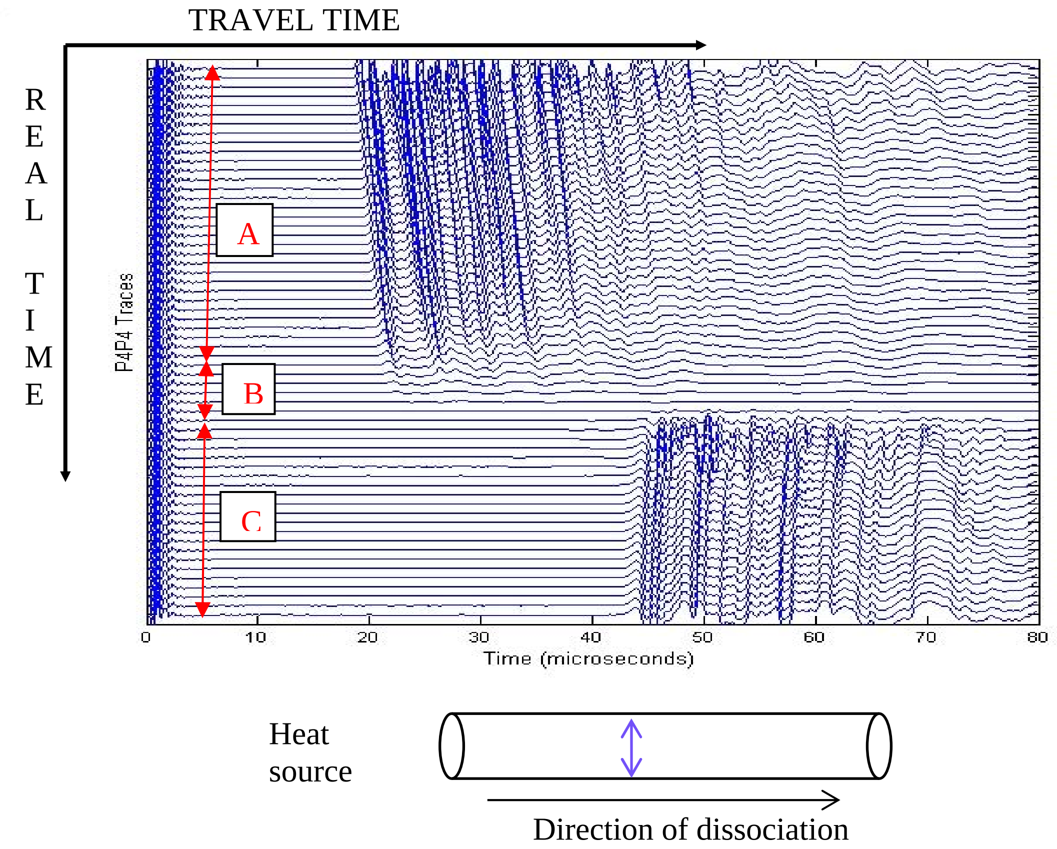


Figure 13. Monitoring of hydrate dissociation in sand pack using a heat source.

Results and Discussion

In this section results from 6 experiments will be presented. In these experiments, samples were prepared using a range of ice/sand ratio with the assumption that the initial ice/sand ratio would represent the hydrate saturation after the conversion of ice to methane hydrate. It is understood that in all cases some unused methane would be present in the pore space and as such the hydrate saturation values would be relative and not absolute values. General characteristics of these samples are shown on Table 1.

Table 1. Initial conditions for synthesized hydrate-staurated samples

Exp #	Ice/Sand volume	Ratio, R	Mixture Porosity
1	0%/100%	0.00	36.50%
2	10%/90%	0.11	37.40%
3	25%/75%	0.33	37.40%
4	30%/70%	0.43	39.50%
5	41.5%/58.5%	0.71	45.60%
6	75%/25%	3.00	44%

Results from velocity measurements on these samples after the completion of the synthesis process are shown on Table 2.

Table 2. Compressional wave velocity for samples with different hydrate saturation as represented by the initial ice/sand ratio.

Ice/Sand (Volume)	Ratio	p11	p22	p33	p44	p55	p66	Average velocity
0/100	0.00	1436.95	1518.15	1486.49	1505.06	1506.04	1506.04	1493.12
10/90	0.11	1616.15	1549.47	1511.58	1531.46	1493.16	1523.11	1537.49
25/75	0.33	1883.26	2041.80	2047.19	2017.62	2197.23	2057.44	2040.76
30/70	0.43	2296.94	2340.82	2450.88	2516.21	2345.53	2123.75	2345.69
41.5/58.5	0.71	2665.01	2807.48	2740.29	2721.08	2776.23	2769.63	2746.62
75/25	3.00	2460.37	2939.81	2499.11	3068.98	2918.93	2815.40	2783.77

It is interesting to note that the compressional wave velocity approaches the maximum value at about 70% hydrate saturation and does not exceed that value by much even for 300% saturation (Figure 13), however, it appears that the shear velocity reaches the maximum when hydrate becomes the dominant phase (Figure 14).

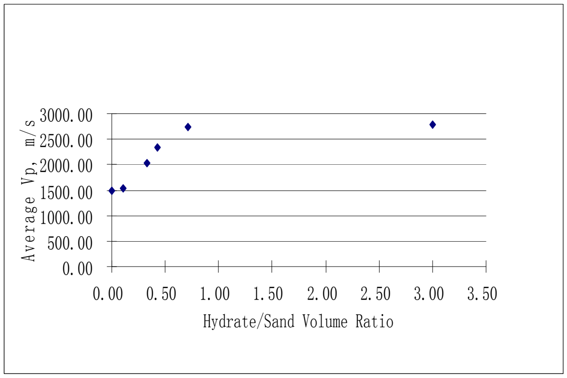


Figure 13. Average P wave velocity at various hydrate saturations.

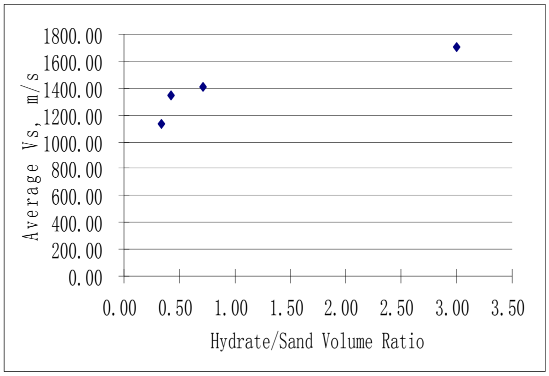


Figure 14. Average S wave velocity at various hydrate saturations.

It is also interesting to note that at higher hydrate saturation a slight decrease in the Vp/Vs ratio occurs (Figures 15 and 16).

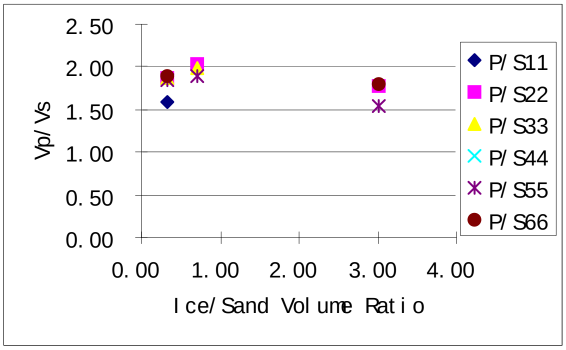


Figure 15. Vp/Vs ratio at various hydrate saturations.

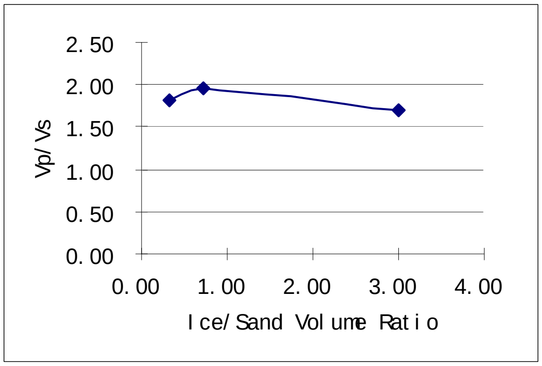


Figure 16. Average Vp/Vs ratio at various hydrate saturations.

Conclusions

- Established a unique laboratory capable of synthesizing different hydrate-impregnated sediments and measurement of their acoustic properties under controllable pressure and temperatures.
- Developed laboratory method for real-time monitoring of hydrate dissociation through ultrasonic measurements. Once a comprehensive data set for dissociation rates for various host rocks is established, it would be possible to model flow properties of hydrate-bearing sediments at reservoir scale.
- Data suggests that acoustic velocity increases as a function of hydrate volume percentage increase and once hydrate volume percentage exceeds 40%, the P wave velocity remains almost unchanged and S wave velocity increases at a low rate. This implies that it is very unlikely that precise hydrate saturation can be inferred from seismic events.
- Data from this laboratory may be used for seismic and sonic inversions and calibration of numerical reservoir simulators.

Recommended Additional Reading and References

Recent worldwide interest in research and development on natural gas hydrates as an energy resource has created a wealth data, information, and knowledge on methane hydrates. Nearly all publicly available data are accessible on the Internet. The US National Energy Technology Laboratory Methane Hydrate Newsletter site (www.netl.doe.gov/scng/ydrate) provides the latest news and information on nearly all major activities and is highly recommended. The publications listed below are strongly recommended for additional reading.

Sloan, E. Dendy, Jr., "Clathrate Hydrates of Natural Gases", Second Edition, Marcel Dekker, Inc., New York, New York, 1997.

Makogon, Yuri F., "Hydrates of Hydrocarbons", PennWell Books, Tulsa, Oklahoma, 1997.

Max, Michael D., Editor, "Natural Gas Hydrate in Oceanic and Permafrost Environment", Kluwer Academic Publishers, 2000.

National Research Council of the National Academy, “Charting the Future of Methane Hydrate Research in the United States”, The National Academies Press, Washington, D.C.

Timothy, S. Collet, “Energy Resource Potential of Natural Gas Hydrates”, AAPG Bulletin, v. 86, no. 11 (November 2002), pp. 1971–1992.