ABSTRACT

Initial and proposed efforts to determine some of the physical characteristics of the massive gas hydrate recovered from Site 570 are described. Sample chamber fabrication and preservation techniques are detailed from the time of shipboard sampling until the sample distribution to various investigators.

The properties considered are heat capacity; heat of dissociation; thermal conductivity; dissociation rate; thermal expansion; acoustic velocity; electrical resistivity; hardness; elastic wave velocity; isotopes of carbon deuterium, and oxygen; chlorinity of hydrated waters; gas composition; ratio of water to methane; pressure changes on gas decomposition; ratio of hydrogen in guest molecules to water; dynamic viscosity and elastic modulus; mineral content of sediment; and liquid water content and location. Participants in the shore-based experiments include the following institutions: U.C. Geological Survey; University of California, Los Angeles; Texas A&M University; Standard Oil of Ohio; National Bureau of Standards (Boulder); Department of Energy (METC); and the Colorado School of Mines.

INTRODUCTION

Naturally occurring gas hydrates may represent a vast, untapped energy source. Their existence in permafrost regions and in suboceanic environments had been well documented, yet until the work of the present report, no samples of hydrate had been recovered for detailed experimental analysis in shore-based laboratories. Such analyses should be aimed at identifying the extent of the resource and determining methods of producing gas from the hydrates. The following work was undertaken with these goals in mind.

In anticipation of encountering natural gas clathrate hydrates on Leg 84, four sample cylinders were fabricated at the Colorado School of Mines. These sample cylinders were made from Air Force surplus 304 stainless steel oxygen containers, which were modified with flanges, fittings, pressure gauges, and relief valves, with dimensions as shown in Figure 1. Each cylinder was hydrostatically tested and the relief valve was set at 3435 kPa. These cylinders were placed aboard ship prior to departure and stored in a shipboard freezer at 263 K.

At Site 570 drilled in a water depth of 1718 m, a core of massive gas hydrate was encountered. The core of almost pure gas hydrate measured 1.05 m in length and 5.6 cm in diameter. This core is not only the first massive gas hydrate ever to be observed in ocean sediment, it is also the first sample of marine gas hydrate to be preserved for shore-based studies. The gas hydrates were placed inside three of the sample cylinders and returned to the freezer. On return to port the three cylinders were transported via surface to the Colorado School of Mines (CSM) in containers refrigerated by dry ice. The fourth cylinder, which had been partially filled with a much smaller amount of hydrate from Site 568, had a sample which did not survive the transportation procedure from shipboard to laboratory. About 0.5 m of core survived in the other three cylinders.

Once in the laboratory the cylinders were immersed in a refrigerated aqueous solution of ethylene glycol and visually inspected for leaks at 253 K. After passing the leak check the cylinders were continuously refrigerated at 230 K. On May 7, 1982, the cylinders were cooled further in dry ice, and given a cursory inspection. Figure 2 is a photograph of one of the hydrate cylinders at that time.

On March 29 through 30, 1982, the U.S. Department of Energy, Morgantown Energy Technology Center (METC), hosted a conference entitled "Methane Hydrates Workshop" to consider the feasibility of hydrates as an unusual gas resource. At that conference proposals were solicited from all attendees for the allocation of the DSDP hydrate samples to various laboratories. An informal proposal review process was determined by the author and K. A. Kvenvolden (USGS). Each proposer agreed to publish the results in a timely manner and to recognize DSDP as the source of the sample, if he/she were to receive a portion of the sample. The proposals received for experiments on the hydrates are detailed in Table 1.

METHODS, RESULTS, AND CONTINUED WORK


A series of three experiments, described in detail by Kvenvolden et al. (in press), were undertaken to establish, under controlled laboratory conditions, some chemical and physical properties of the preserved gas hydrate. Specifically, the purposes of the experiments were to determine the composition of the major components of the gas mixture, to measure the ratio of methane to water, and to demonstrate the pressure changes the gas hy-
Table 1. Shore-based experiments on Site 570 hydrates.

<table>
<thead>
<tr>
<th>Institution</th>
<th>Principal investigator</th>
<th>Measurements</th>
<th>Status</th>
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<tr>
<td>Colorado School of Mines</td>
<td>E. D. Sloan</td>
<td>1. Heat capacity</td>
<td>In progress</td>
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<td>2. Heat of dissociation</td>
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<td>3. Dissociation rate</td>
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<td>4. Thermal conductivity</td>
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<td>Department of Energy (METC)</td>
<td>R. D. Malone</td>
<td>1. Acoustic velocity</td>
<td>In progress</td>
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<td></td>
<td></td>
<td>2. Electrical resistivity</td>
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<tr>
<td>(Boulder)</td>
<td></td>
<td>2. Thermal conductivity</td>
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<td>3. Thermal expansion</td>
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<td>4. Heat-flow studies</td>
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<td>5. Fracture resistance</td>
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<td>6. Hardness</td>
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<td>7. Elastic wave velocity</td>
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<td>Standard Oil of Ohio</td>
<td>R. L. Horton</td>
<td>1. Pulsed NMR spectroscopy</td>
<td>In progress</td>
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<td>2. Mechanical properties</td>
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<td>3. Focused acoustic attenuation</td>
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<td>4. Broad-band microwave attenuation</td>
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<td>Texas A&amp;M University</td>
<td>J. M. Brooks</td>
<td>Carbon isotopes for: methene, ethane, carbon dioxide</td>
<td>Complete</td>
</tr>
<tr>
<td>University of California, Los Angeles</td>
<td>B. Barracough</td>
<td>1. Deuterium analysis</td>
<td>Complete</td>
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<td>2. Oxygen isotopic analysis</td>
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<td></td>
<td>3. Chlorinity</td>
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<td></td>
<td>2. Ratio of water/methane</td>
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<td>3. Pressure changes on gas decomposition</td>
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Pressure changes resulting from the intermittent release of gas during decomposition of this gas hydrate at 277 K follow a characteristic pattern that is diagnostic for gas hydrates in general as discussed by Hunt (1979, pp. 160–161). The equilibrium pressure for this hydrate...
was estimated to be between 3800 and 3900 kPa. This pressure is in the same range as the equilibrium pressure at 277 K of 3810 kPa for a pure methane-pure water system given by Deaton and Frost (1948).

University of California, Los Angeles (B. Barracough)

Clathrate meltwater was analyzed for hydrogen and oxygen isotopes (18) and for chlorinity with the following results:

\[ \delta D (\text{SMOW}) = +18\%o \pm 1.0 \]
\[ \delta^{18}O (\text{SMOW}) = +2.0\%o \pm 0.2 \]
\[ Cl = 0\%o \] (J. Gieskes, personal communication, 1982)

Although some calculations have been made to determine the isotopic composition of the original porewater and the fractionation factors for oxygen and hydrogen in natural clathrate-porewater systems, it will be necessary to obtain continuous chemical and isotopic profiles at Site 570 before these values can be reliably modeled. Examination of these values does indicate that the clathrate lattice concentrates the heavier isotopes, a behavior that was expected from thermodynamics, and by analogy with normal hexagonal ice.

The low-chlorinity value is indicative of pure water, which suggests that essentially all of the water sample was bound in the clathrate lattice and that contamination caused by mixing of trapped remnants of the original porewater is negligible. The question of where all of the salts have gone awaits resolution.

Texas A&M University (J. M. Brooks)

Carbon isotopes for methane, ethane, and carbon dioxide were measured, with results as follows:

\[ \delta^{13}CH_{4} = -44.0\%o \] (PDB)
\[ \delta^{13}C_{2}H_{6} = -26.7\%o \] (PDB)
\[ \delta^{13}CO_{2} = -2.9\%o \] (PDB)

These measurements indicate that the methane is abiotic (J. M. Brooks, et al., this volume)

Standard Oil of Ohio (R. L. Horton)

Four areas of research are in progress as follows.

Pulsed NMR Spectroscopy

NMR (nuclear magnetic resonance) work has been done on laboratory-synthesized hydrates (Davidson et al., 1977), but there may be interferences in naturally occurring samples resulting from paramagnetic impurities. The goal of this work is to determine the relative hydrogen content in the sample because of (1) guest molecules and (2) water. The pulsed Fourier transform NMR spectrometer is in place and operational. Studies are currently directed toward sealing the hydrate in a sample tube.

Mechanical Characteristics

Dynamic viscosity and elastic modulus will be compared among hydrates, permafrost, and ordinary sedimentary rocks from the liquid nitrogen normal boiling point to 190 K. The mechanical spectrometry instrumentation is in place, but the design and fabrication of the sample holder has yet to be accomplished.

Focused Acoustic Attenuation

These tests are aimed at determining mineral content of hydrate in sediments. The tests are also nondestructive. The acoustic equipment necessary to conduct this test is in place and operational; however, the apparatus also lacks a sample holder.

Broadband Microwave Attenuation

This test is for liquid water content and location in conventional hydrocarbon and water-laden cores. Preliminary evidence suggests that hydrate may be distinguished from ice and liquid water with this method. The equipment has been specified and a request for purchase authorization has been made.

All of this research is both nondestructive and non-discretionary and will be published in a timely manner.

National Bureau of Standards, Boulder (J. E. Callanan)

Proposals have been submitted to the Department of Energy (DOE) and the Gas Research Institute (GRI) for work with the portion of the sample of natural gas hydrate from Site 570 that was allocated to the National Bureau of Standards. The proposal as submitted calls for preparative work with artificial hydrates utilizing the equipment and conditions that will exist in the study with the natural sample.

Proposed studies on the natural sample include a series of heat-capacity measurements designed to evaluate repeatability of the measurements and homogeneity (or lack of it) of the sample. Heat-capacity measurements will also be made at elevated pressures. Thermal-conductivity and thermal-expansion measurements will be made up to 195 K in a manner that will detect anisotropy, if present.

Heat-transfer studies, both transient and steady state, will yield heat-flow information and, by following heat effects accompanying dissociation and gas evolution, give information about hydrate stability and rates of decomposition.

Strength properties of the sample will be evaluated with conventional compression testing procedures; fracture resistance, hardness, and elastic wave velocity will also be measured.

Modeling, at the molecular level, of the heat capacity and thermal conductivity is proposed. Descriptive models for the experimental work will be developed. In addition, the stability of hydrate structures as functions of temperature, pressure, and of guest species concentration and variability will be investigated.

Morgantown Energy Technology Center (R. D. Malone)

The objective of this work is to measure the electrical resistivity and sonic velocity of the in situ sample. A special vessel, consisting of a 10.1-cm-ID stainless steel nipple with two flanges, has been specifically designed
for each experiment. Sample transfer and cutting practice has been obtained on both tetrahydrofuran (THF) and methane hydrate. The experimental technique requires parallel faces for the sample; the current work is devoted to exploring means of obtaining such parallel faces. Any pieces of the core removed during cutting will be recovered for a number of possible tests including gas chromatography, spectroscopic, and X-ray analyses.

Preliminary measurements indicate the acoustic velocity is 3.0 km/s, whereas the electrical permittivity is comparable to that of ice over the range for 10 to 20,000 Hz.

Colorado School of Mines (E. D. Sloan)

The objective of this work is to determine the heat capacity, heat of dissociation, dissociation rate, and thermal conductivity of the Site 570 Samples. The effect of various sediments (glass beads, Ottawa sand, and Blake-Bahama Ridge sediment) on THF hydrate heat capacity and heat of dissociation has been determined in preliminary experiments; for these a Differential Scanning Calorimeter (DSC) has been interfaced with an Apple II microprocessor (Rueff, 1983). The modification of the DSC for high-pressure sensing, in addition to the normal temperature sensing and heat input, is currently in progress to support measurements on the in situ samples.

A Cahn microbalance is in the initial stages of fabrication to measure the mass change of hydrate, along with pressure, as a function of heat input. Moving-boundary (ablation and two region) models have been developed to describe the rate of hydrate dissociation. Physical parameters for the model will be provided by the DSC, microbalance, and thermal conductivity experiments as checks on the model.

Solid thermal-conductivity measurements will be made on the samples, using the hot probe method of Von Herzen and Maxwell (1959). The probe has been designed, fabricated, and tested on THF hydrates. Microprocessor A/D interfacing with the probe will enable experimentation on various solids and sediments before testing the in situ samples.

SUMMARY

Shore-based studies of Site 570 hydrates are just beginning to yield results, with experiments that will continue over a time period of a few years, as just detailed. All of the information obtained on the hydrates will be available to the public in a timely manner. Because of the paucity of data on these hydrates it is important to duplicate several experiments in various labs to determine both accuracy and precision of the measurements, as well as the integrity of the sample.

ACKNOWLEDGMENTS

The author gratefully acknowledges the following persons, both for participating in the study of the hydrate samples and for providing the information that is the basis of this report: R. D. Malone (DOE-METC), K. A. Kvenvolden and G. E. Claypool (USGS), J. E. Callanan (NBS-Boulder), R. L. Horton (SOHIO), J. M. Brooks (Texas A&M), and B. Barraclough (UCLA).

Dr. W. R. Parrish of the Phillips Petroleum Company and Professor G. D. Holder of the University of Pittsburgh kindly consented to review this chapter.

REFERENCES


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