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TECHNOLOGY STATUS REPORT**

Gas Hydrates

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PREFACE

This report describes the state of the art in technology on the subject resource, a part of DOE's research program on unconventional gas recovery. It discusses the technical issues warranting investigation and focuses on current activities that are being supported by DOE. As presented, it is intended to provide an in-depth perspective of the knowledge base required to develop concepts for recovery. As new information becomes available, it will be summarized annually. This will permit timely transfer to the private sector.

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EXECUTIVE SUMMARY

In 1983, the U.S. Department of Energy (DOE) assumed the responsibility for expanding the knowledge base and for developing methods to recover gas from hydrates. These are ice-like mixtures of gas and water where gas molecules are trapped within a framework of water molecules. This research is part of the Unconventional Gas Recovery (UGR) program, a multidisciplinary effort that focuses on developing the technology to produce natural gas from resources that have been classified as unconventional because of their unique geologies and production mechanisms.

Current work on gas hydrates emphasizes geological studies; characterization of the resource; and generic research, including modeling of reservoir conditions, production concepts, and predictive strategies for stimulated wells. Complementing this work is research on in situ detection of hydrates and field tests to verify extraction methods. Thus, current research will provide a comprehensive technology base from which estimates of reserve potential can be made, and from which industry can develop recovery strategies.

Private funding for gas hydrates research and development (R&D) is insufficient for several reasons: (1) the usefulness of gas hydrates as an energy source is still hypothetical, (2) immediate and future gas requirements are expected to be constant, and (3) the U.S. still relies heavily on imports. The U.S. DOE is providing leadership for research in gas hydrates and coordinates its activities with academia, industry, private groups, Federal agencies, and their foreign counterparts. In response to this need, the DOE's Morgantown Energy Technology Center (METC) implemented a gas hydrates R&D program that emphasized an understanding of the resource through (1) an assessment of current technology, (2) the characterization of gas hydrate geology and reservoir engineering, and (3) the development of diagnostic tools and methods. Recovery of natural gas from gas hydrates will be made possible through (1) improved instrumentation and recovery methods, (2) developing the capability to predict production performance, and (3) field verification of recovery methods.

Gas hydrates research has focused primarily on geology. As work progressed, areas where gas hydrates are likely to occur were identified, and specific high potential areas were targeted for detailed investigation. A Geologic Analysis System (GAS) was developed. GAS contains approximately 30 software packages and can manipulate and correlate several types of geologic and petroleum data into maps, graphics, and reports. The system also contains all well information currently available from the Alaskan North Slope area. Preliminary mapping of hydrate prospects for the Alaskan North Slope is underway.

Laboratory research on gas hydrates includes the characterization of the physical system, which focuses on creating synthetic methane hydrates and developing synthetic hydrate cores using tetrahydrofuran (THF), consolidated rock cores, frost base mixtures, water/ice-base mixtures, and water-base mixtures. Laboratory work produced measurements of the sonic velocity and electrical resistivity of these synthetic hydrates. During 1983, a sample from a natural hydrate core recovered from the Pacific coast of Guatemala was tested for these properties by DOE/METC. More recently, natural hydrate samples acquired from the Gulf of Mexico have been tested.

Modeling and systems analysis work has focused on the development of GAS and preliminary gas hydrate production models. Models were developed for both steam injection and reservoir depressurization methods of gas production from gas hydrates. Concepts for in situ combustion production and for combining the thermal and depressurization concepts were also developed.

The natural gas hydrate cores will continue to be tested for thermal properties, dissociation properties, fracture mechanics, and optical properties. More sonic velocity and electrical resistivity measurements will be obtained. These activities will include a more detailed study of the Alaskan gas hydrate deposits. Research in the Gulf of Mexico and other target areas has also been initiated. Long-term plans include the determination of diagnostics for hydrate detection, and the development of predictive techniques to forecast production. As this work progresses, field testing and verification activities will be performed. Through the successful completion of these activities, the potential of gas hydrates as a natural gas resource will be assessed, and the technology necessary for the development of the resource will become available.

1.0 INTRODUCTION

Gas hydrates are a type of inclusion compound, or clathrate, formed as a solid, ice-like mixture of gas and water where gas molecules are trapped within a framework of water molecules. Water and natural gas, under certain conditions of temperature and pressure, can form naturally occurring gas hydrates in sediments that underlie ocean basins and permafrost regions. Once formed, these deposits are very stable and can even act as a seal or caprock to prevent seepage of deeper gas accumulations to the Earth's surface.

The first documentation of laboratory experimentation dealing with clathrates is credited to Davy (1811), who reported the formation of a yellow precipitate as a result of chlorine gas bubbling through water. Four stages of research efforts are shown in the chronological history of gas hydrate research (Figure 1). The first stage consisted of a series of purely academic studies. The second stage developed in the 1930's when it was discovered that hy-

drates could form in natural gas transportation lines and effectively block the gas flow. At this point, research efforts shifted from the purely academic to more practical research, and focused on devising methods to prevent hydrate formation in gas pipelines in cold regions.

The third stage of research began in the 1950's and 1960's when unusual drilling experiences in Arctic and offshore operations led to the speculation that hydrates could exist in nature and could represent a potential gas resource. This stage resulted in a series of studies focused on phase behavior relationships, pressure and temperature curves, and speculations of naturally occurring gas hydrate deposits. The third stage culminated in the late 1960's when Soviet scientists announced the discovery and recovery of hydrate crystals from sedimentary formations in Siberia. This announcement initiated the fourth and current stage of gas hydrate research. This stage of research has focused on effort to evaluate the potential of gas hydrate formations as a future energy supply.

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FIGURE 1. HISTORICAL EVENTS IN GAS HYDRATE RESEARCH

2.0 STATE OF TECHNOLOGY

The scientific and technological factors that impact or influence the production of gas from gas hydrate reservoirs are described and discussed in the following sections of this document; these factors form the basis for DOE research on the subject.

2.1 PHYSICAL PROPERTIES RESEARCH

While the current knowledge base on the physical property characteristics of clathrates is fairly complete, the physical properties of one class of clathrates, gas hydrates, are only now beginning to be understood in the laboratory. Research efforts to determine the physicochemical properties have focused on electrical resistivity and sonic velocity, as well as on an attempt to understand how hydrates form in the natural environment. Laboratory experiments on both natural and man-made gas hydrate samples will provide the basic data for the development of (1) reservoir models, (2) diagnostic techniques, and (3) production techniques. Work to date on property determinations has been undertaken by the Gas Research Institute (GRI), DOE, the Canadian and Russian governments, and several universities.

Major accomplishments to date include the following:

- Synthetic samples of methane hydrates have been successfully made.
- Electrical resistivity measurements have been successfully made on both natural and synthetic hydrates.
- Sonic velocity measurements have been successfully made on both natural and synthetic hydrates.
- Thermal conductivity measurements have been successfully completed on hydrate samples and indicate a measurable difference between gas hydrates and ice.
- Thirty experiments on hydrate dissociation, which provides useful data for production modeling development, have been completed.

2.2 GEOLOGICAL RESEARCH

The current knowledge of gas hydrate geology is inadequate to provide direction for reservoir analysis and stimulation research. This geology is complex and poorly understood in both onshore and offshore formations. Prior studies relative to the geology of gas hydrate localities were primarily indirect studies that arose from problems involving unexpected gas releases and blow-outs in industry wells; these studies were mostly conducted by GRI and the U.S. Geological Survey (USGS). Current DOE research efforts have focused on the geology that is directly related to gas hydrate deposits in areas where conditions favor the formation of hydrates. The purpose is to obtain data that will enable researchers to understand hydrate deposits and to develop diagnostic criteria to define a hydrate reservoir and its geometry.

Major accomplishments to date include the following:

- Cores of gas hydrates have been obtained from wells in the Gulf of Mexico and offshore Guatemala.
- Eight basins have been analyzed for their potential for gas hydrate occurrences.
- Geologic cross-sections of potential hydrate-bearing zones in the Alaskan North Slope have been prepared.
- The onshore data collection phase for gas hydrates has been initiated and geologic samples have been obtained for study.
- Preliminary geologic analysis of two onshore areas (National Petroleum Reserve Alaska [NPRA] and Prudhoe Bay/Kuparuk Field) have been completed.

2.3 DIAGNOSTICS RESEARCH

Diagnostics criteria and development of instrumentation will enable researchers and industry to locate and define hydrate reservoirs and their corresponding geometry. Research in this activity has been very limited to date. Plans are to increase the research effort for diagnostics in the future. Current accomplishments for diagnostics include the following:

- A preliminary evaluation has been made of commercial subsurface logging equipment and the potential for such equipment to identify gas hydrate deposits. Data are currently inconclusive.
- A preliminary evaluation has been made of surface geophysical techniques and their potential for gas hydrate detection. Seismics and electromagnetics appear to be potentially useful.

2.4 PRODUCTION TECHNOLOGY RESEARCH

Current research activities for production technology have been limited to production modeling and preliminary economics. Several production concepts have been identified; however, research efforts remain inadequate at this time for predicting production quantity and quality from gas hydrate reservoirs, as well as inadequate for more than preliminary gas-in-place estimates.

Major accomplishments to date include the following:

- Conceptual models have been completed for continuous thermal recovery, cyclic thermal recovery, depressurization, and in situ combustion for production of gas from gas hydrates.
- A mathematical model has been developed for thermal recovery of gas from gas hydrates.
- A preliminary finite difference model has been developed for gas recovery from gas hydrates through reservoir depressurization.
- Preliminary gas-in-place estimates have been made for hydrates on Alaska's North Slope.
- Preliminary gas-in-place estimates have been made for five areas of the U.S. continental margin.

3.0 TECHNOLOGY DESCRIPTION

Research has indicated that at least four factors must be present before hydrates can form: (1) low temperatures, (2) high pressures, (3) water, and (4) gas. Structural lattice studies indicate that both gas and water constituents are required to form the hydrocarbon clathrate or hydrate. Studies have

shown that two structures are possible. These structures are termed Structure I and Structure II, and are described in more detail in Section 4.1.1 of this report. The Structure I lattice is the most common, and is primarily composed of methane or ethane hydrocarbon gases, while the Structure II contains appreciable quantities of propane and isobutane hydrocarbon gases. Both structures can and do contain trace quantities of other gases such as hydrogen sulphide or nitrogen.

Based on the size of the unit cells of each structure, and based on the gas molecules required to develop the Structure I or Structure II cavities, approximately 6 moles of water are required for every mole of gas to completely fill all of the cavities within the unit cell of a hydrate structure. By applying these gas/water ratios to the geological environment, one of two possible situations can occur.

- All of the gas within the reservoir could be locked-up in the hydrate structure, leaving no free gas. However, there is water within the formation (or ice if the temperatures are below the freezing point). This situation is called a *water-dominated system*.
- All available water is used to build the hydrate lattice, providing a formation with no water and free nonhydrated gas. This situation is referred to as a *gas-dominated system*.

Research efforts have indicated that gas migrating upwards from a deeper source rock does not require a structural or stratigraphic trapping mechanism to form hydrates. Once gas has entered the hydrate stability zone (HSZ) and encounters water or ice, hydrates will form. Figure 2 indicates the location of the hydrate stability zone for pure methane gas. The inclusion of ethane, propane, isobutane, or a combination of these will increase the zone of hydrate stability. However, it is not known how far into the HSZ the gas migrates before the hydrate begins to form. Two systems are possible.

- If hydrate formation begins immediately, hydrates can form a layer at the base of the HSZ. Over a period of time this can result in an impermeable layer that effectively traps free gas beneath the hydrate layer. When this occurs in an area that is solely dependent upon upward-migrating gas for hydrate formation, it is referred to as a *closed system*.
- If there are gas source rocks within the HSZ, and if gas is generated regardless of the hydrate layer formed at the base of the HSZ,

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FIGURE 2. GAS HYDRATE STABILITY ZONE

hydrates can form anywhere within the HSZ. This situation is referred to as an *open system*.

The types of hydrate deposits can be classified. Based on photographic evidence of recovered gas hydrate samples from the Gulf of Mexico, Blake Outer Ridge, Guatemala, and Canada, there are four distinct types of gas hydrate deposits: (1) *disseminated* (crystalline), (2) *nodular*, (3) *layered*, and (4) *massive*. (See Figure 3.) The disseminated and nodular types are common, and the layered and massive types are less common. It has been postulated that disseminated gas hydrates are first deposited; as gas is added to the system, the disseminated crystals act as seed crystals for further growth called nucleation. As nucleation proceeds and the hydrate deposits grow, the disseminated or seed crystals form nodules of much larger size. However, these nodules are still dispersed throughout the sediment matrix. The expansion of the crystals as they grow creates fractures within the sediment body that permits lateral growth of the hydrates. Over time and with sufficient gas and water, these nodules

may connect and form layered hydrates nestled between layers of sediment. The massive hydrate could form in one of two ways: (1) the layered hydrate could continue to nucleate, expanding to incorporate the layers of sediment within the hydrate and eventually forming thick massive bodies of gas hydrate deposits of almost pure hydrates; and (2) the nodular hydrate could continue to nucleate until large massive bodies of gas hydrate deposits form.

Recognizing that gas hydrates form under conditions of relatively low temperature and high pressure, two opposing factors control the distribution of hydrates in the Earth. The first is the geothermal gradient, or temperature increase associated with increasing crustal depth. Average continental gradients are generally 70 to 80°F/mi, although this range can be highly variable. Oceanic crustal gradients are less well known but are roughly analogous. Because hydrates are stable under conditions of relatively low temperature, the geothermal gradient limits hydrate formation to shallow, cooler regions

DISSEMINATED

NODULAR

LAYERED

MASSIVE

FIGURE 3. GAS HYDRATE DEPOSITIONAL FORMS

of the crust. The second factor that controls the distribution of hydrate regimes is the increase of pressure with greater depth, within the defined boundaries indicated on Figure 2.

Increased pressure tends to favor the formation of hydrates at greater depths where temperatures are relatively higher. Figure 2 shows the pressure/temperature/depth relationships that are conducive to the formation of gas hydrates. The HSZ defines the limits for possible formation of natural gas hydrate to the interval from approximately 900 to 4,000 feet at temperatures between +12 and -8°C. These zones can occur in or adjacent to onshore permafrost areas of Alaska, Canada, and other cold regions. Other major areas of potential hydrate formation exist in the sediments of the world's ocean basins. Current theory on offshore HSZ's holds that formation conditions are favorable in areas where the water depth exceeds approximately 1,500 feet; however, actual hydrate formation depths are unknown.

The potential for gas hydrate occurrence in permafrost regions has been postulated based on unusual drilling experiences, wireline logs, and core behavior as reported by drilling companies working in Prudhoe Bay, Alaska; the Mackenzie Delta, Northwest Territories; and the Arctic Archipelago, Canada. Other observations such as variations in electrical resistivity, bubbling and gas exhalations from cores, intermittent gas flows from wells, exploding core barrels, and dramatically improved gas production from wells that were treated with methanol, all serve as evidence that such deposits are composed of gas hydrates.

Because of the pressure/temperature conditions and the geothermal gradient, a terrestrial HSZ can occur only in or near continental permafrost regions at depths greater than 800 to 900 feet. Permafrost covers more than 23 percent of the Earth's landmass, and is restricted chiefly to Canada (63 percent), Alaska (75 percent), the U.S.S.R. (47 percent), Scandinavia, Greenland, and Antarctica.

Because of low average surface temperatures in these regions, the geothermal gradient is depressed, making it possible to have sufficiently low temperatures at depths great enough to stabilize hydrates. If the average annual surface temperature or the actual geothermal gradient for a particular area is known, it is possible to determine whether conditions at depth are favorable for gas hydrate stability.

If so, the potential thickness of the sedimentary section with hydrate potential can be determined. For purposes of research in the Alaskan North Slope area, a depth of 5,000 feet has been arbitrarily chosen as the lower limit of potential hydrate occurrence.

Natural gas hydrates are also thought to occur beneath the world's seas and oceans where a water column of approximately 1,500 feet exists and where temperatures are appropriate for hydrate stability. These conditions are met in more than 90 percent of the ocean basins.

Average thicknesses of the HSZ for the oceans are not well known. The bottoms of probable hydrate deposits have been detected by means of drilling and seismic profiling at depths in excess of 1,000 feet, indicating the possibility of considerable vertical development of the HSZ in the marine environment, if the region of hydrate formation extends up to the ocean/sediment interface. Table 1 indicates the estimated thicknesses of the HSZ obtained during the basis analysis studies.

TABLE 1. THICKNESS OF THE HYDRATE STABILITY ZONE (HSZ) IN POTENTIAL HYDRATE AREAS

LOCATION	HSZ THICKNESS (feet)
Blake-Bahama Outer Ridge	1,300
Gulf of Mexico	650-2,950
Newfoundland/Labrador Area	200-1,970
Panama Basin	820-1,800
Baltimore Canyon	1,450-1,900
Northern California Offshore	620-750
Columbia Basin	980-6,550
Alaskan North Slope	980-5,000

Current research activities are directed toward an understanding of the depositional features conducive to hydrate formation in the natural environment.

4.0 CURRENT ACTIVITIES

4.1 PHYSICAL PROPERTIES RESEARCH

Data obtained through laboratory testing and experimentation on both synthetic and natural gas hydrate samples are being compiled, integrated, and interpreted to provide an understanding of both the characteristics of hydrate formation and the characteristics of hydrate dissociation. These physical, chemical, thermal, and mechanical properties will also provide the basis for (1) diagnostics of hydrate deposits, and (2) the techniques necessary for the development of technical and economic production of gas from hydrate deposits.

4.1.1 Formational Characteristics

Methane hydrates form as a white, ice-like crystalline substance composed of hydrate complexes. The hydrate crystal has been described as a solid, cage-like structure formed by water that physically entraps gas molecules in structural voids or cavities. Hydrates that form from constituents commonly found in natural gas have one of two crystalline structures. Structure I is the most common and occurs when the physical dimensions of the gas molecules are 5 Å (i.e., methane, ethane, CO₂, and H₂S). If larger diameter molecules are present (be-

tween 5 and 6.9 Å), Structure II is formed. Molecules larger than isobutane cannot fit into the cavities and do not form hydrates. Gases such as hydrogen or helium are small enough to pass between the cavities of the structure and do not form hydrates. The nature of the interaction between the host (water) and the guest (gas) molecules is not completely understood, but it is suggested that a simple Van Der Waals interaction model is not sufficient to explain the necessary lattice stabilization energies and some of the physical and chemical properties of the clathrate.

Laboratory investigations have shown that propane enters only the largest cavities of a Structure II hydrate, which has an average diameter of 9.46 Å. The smaller cavities of a Structure II hydrate have an average diameter of 7.82 Å and do not encage propane molecules. The largest cavity of a Structure I hydrate is only 8.60 Å, which is probably too small to be stabilized by propane. This is why propane forms Structure II hydrates.

Conversely, ethane is known to enter only the large cavities of Structure I hydrates and is too large to stabilize the hydrates of either structure by entering the small cavities. The large cavity of a Structure II hydrate is too large for ethane to contribute much stabilization to the surrounding water molecules by entering this cavity. Table 2 shows the ratio, R, of

TABLE 2. COMPARISON OF DIAMETERS OF METHANE, ETHANE, AND PROPANE TO THE FREE DIAMETERS OF CAVITIES IN STRUCTURE I AND STRUCTURE II HYDRATES

MOLECULE	STRUCTURE	HYDRATE CAVITY	$R = \frac{\text{MOLECULAR DIAMETER}}{\text{FREE CAVITY DIAMETER}}$
Methane (CH ₄)	I	Large	0.575*
	I	Small	0.649*
	II	Large	0.504
	II	Small	0.659
Ethane (C ₂ H ₆)	I	Large	0.652*
	I	Small	0.737
	II	Large	0.571
	II	Small	0.748
Propane (C ₃ H ₈)	I	Large	0.741
	I	Small	0.837
	II	Large	0.649*
	II	Small	0.849

*These cavities are occupied in the hydrate molecule, which occurs from a binary mixture of the indicated alkane and water as determined by hydrate numbers of the crystals and assuming that the molecular diameter of water is 2.50 Å.

the molecular diameter to the free cavity diameter for occupancy of the various hydrate cavities by methane, ethane, or propane. The free cavity diameter is only the cavity diameter minus the diameter of a water molecule, since the cavity diameter is measured from the center of one water molecule to the center of the water molecule on the other side of the cavity. (Note: A molecule never occupies a cavity when the value of R is greater than 0.7 and *all* cavities normally occupied have a value of R that is very close to 0.65.)

For an ethane molecule going into the large cavity of a Structure I hydrate, the value of R is 0.652 and the average center-to-center intermolecular separation, r , is 4.3 Å. For the large cavity of a Structure II hydrate, R is 0.571 and the average intermolecular separation, r , is 4.73 Å. Although this difference may seem slight, it is significant because the intermolecular potential function is proportional to r^{-6} . For this example, where ethane is occupying the large cavities of a Structure I hydrate, r^{-6} is $(6,320 \text{ Å})^{-6}$ and where ethane is occupying the large cavities of a Structure II hydrate, r^{-6} is $(11,200 \text{ Å})^{-6}$, or nearly a two-fold increase. Using Table 2, several observations can be made regarding the occupancy of the various cavities by methane, ethane, and propane.

- The only cavity that propane can enter is the large cavity of a Structure II hydrate. The value of R exceeds 0.74 in all other cavities.
- Ethane can enter the large cavities of either a Structure I or II hydrate, but cannot enter the small cavities of either structure. Ethane stabilizes the Structure I hydrate, where the value of R is 0.652. For a Structure II hydrate, the value of R is only 0.571. Clearly, this is why ethane-water mixtures form Structure I hydrates and not Structure II hydrates.
- Methane can enter both cavities of either structure. Although methane-water mixtures form Structure I hydrates, the values of R appearing in Table 2 do not clearly indicate that Structure I should form in preference to Structure II, since both structures have a cavity whose value of R is near 0.65. This is consistent with the data of Deaton and Frost (1946), which show that less than 1-percent propane in a methane-propane mixture is needed to stabilize a Structure II hydrate in preference to a Structure I hydrate.

Any gas/water system capable of forming a clathrate compound, according to the example

can be thought of as a solid solution of guest molecules in a host lattice. The fractional occupancy (filled voids divided by total number of voids) in a hydrate is determined by pressure, temperature, and partial pressure of the guest at the time of formation. Occupancies of more than 90 percent for a pure methane hydrate are typical. The number of water molecules per guest (n) in the above equation varies from less than 6 for small gas molecules to more than 17 for isobutane. Thus, the yield of natural gas (cubic feet per cubic foot of hydrate) is variable, and depends upon both the fractional occupancy of the void space and the bulk composition of the guest gas.

4.1.2 Physical Property Testing

Phase equilibrium studies have been conducted by numerous investigators on hydrates of various gas compositions. At high pressures and low temperatures, ice and solid gas hydrates will predominate; at high temperatures and low pressures, the formation of gas and liquid water will be favored. (See Figure 2.) The addition of salt to water lowers the temperature of hydrate formation, and in effect shifts the gas hydrate boundary curve to the left. The addition of CO_2 , H_2S , C_2H_6 , or C_3H_8 raises the temperature of hydrate formation, shifting the gas hydrate curve to the right. Therefore, impurities in natural gas will alter the area of the hydrate stability field. The degree of alteration is dependent on the quantity and type of impurity. However, the effects of these impurities in the natural environment are largely unknown at this time.

The direction of laboratory experimentation is now aimed toward the definition of the physical and chemical properties of gas hydrates in synthetic (laboratory-prepared) cores. Some investigators have had success using propane as the lattice guest, while other groups have done extensive work with THF as the lattice guest. Because of the high-pressure, low-temperature stability for pure methane hydrate, synthesizing methane hydrate cores has been a challenge to investigators.

There are several handling advantages to working with THF. THF hydrate is stable at ambient pressure for temperatures near 32°F, and accurate stoi-

chiometric mixtures of THF and water can be prepared. The laboratory work is also made easier because THF (a liquid) is miscible in water. However, analogies have yet to be made between physical property measurements using liquid THF, ethylene oxide, and propane hydrates and the physical properties of pure methane hydrates or natural hydrates.

Characterization of the physical system for gas hydrates has been advanced through three significant events: (1) the recovery of natural gas hydrate cores, (2) the development of THF hydrate in a consolidated media, and (3) the development of techniques for synthesizing methane hydrates.

Natural Gas Hydrate Core: The National Science Foundation sponsored the Deep Sea Drilling Project (DSDP), chartered to probe and study the waters and sediments of the world's oceans. In 1980, the DSDP deployed a pressure core barrel in an attempt to collect subsea samples of suspected methane hydrate accumulations off the eastern coast of the U.S. The most significant finding was the documentation of naturally occurring methane hydrates.

In February 1982, the first natural gas hydrate core preserved for laboratory testing was recovered off the west coast of Guatemala, Central America. The core was 3.4 feet in length and consisted of about 93-percent hydrate and 7-percent sediment. The preliminary measurements indicated that the gas composition was 99-percent methane, and 1-percent propane and other gas constituents. The core was recovered from a depth of approximately 2,000 feet. The water column was approximately 1,700 feet with 300 feet of overlying sediment. The total measured thickness of the in-place hydrate zone was 13 feet.

Several organizations were given a portion of this core for experimental purposes. In addition to the Colorado School of Mines and DOE/METC, these organizations were National Bureau of Standards, USGS, Standard Petroleum Company, University of California at Los Angeles, and Texas A&M University.

The sample received by DOE/METC in December 1982 measured approximately 2 inches in diameter and 1.4 inches in length. The sample was maintained at dry ice temperature (-110°F) or liquid N_2 temperature (-320°F) during the laboratory equipment preparation and testing period until it

was removed from the pressure vessel for radiographic analysis. The sample was X-rayed to determine the sedimentary content of the core; the radiographs showed no major sediment inclusions.

Electrical resistivity and acoustic velocity measurement flanges were designed and constructed specifically for the DSDP hydrate sample. The electrical resistivity measurements were completed at three temperatures. The measuring chamber was pressurized to the equilibrium methane hydrate pressure for each temperature in order to prevent dissociation. The experiments showed a general increase in permittivity with an increase in temperature.

The acoustic velocity of the hydrate core at a temperature of $+39.2^{\circ}\text{F}$ was determined to be $10,000 \pm 150$ ft/s. The velocity was determined by measuring the time of flight of a high voltage excitation pulse. Future experiments will include acoustic velocity measurements at several temperatures.

During the spring of 1983, a second core of gas hydrate was recovered for testing at DOE/METC. This core was recovered by Texas A&M University while doing research for an industry consortium in the Green Canyon area of the Gulf of Mexico, off the coast of Louisiana. This core is of the disseminated type (nodular hydrate inclusions within sediment), with a hydrocarbon gas composition of over 50-percent propane and ethane. A sample of this core is being tested in the laboratory and property measurements are being made.

THF Hydrate: The work on developing synthetic hydrate cores progressed significantly when Los Alamos National Laboratory succeeded in forming THF hydrates in samples of consolidated rock cores. Three types of rock were used in developing these synthetic cores: Berea Sandstone, Solenhofen Limestone, and Austin Chalk. The densities and porosities of the three rock cores are shown in Table 3.

The samples were cylindrical cores, cut perpendicular to the bedding planes. The samples were first baked for 24 hours at 212°F in a vacuum oven to remove residual pore water from the rock cores. Because ionic compounds act as inhibitors to hydrate formation and because ionic conduction in a liquid phase can have an important effect on the electrical properties, measured amounts of NaCl varying from 0.05 to 1.0 moles were added to the fluid for various experiments.

TABLE 3. DENSITY AND POROSITY OF CONSOLIDATED ROCKS USED IN SYNTHETIC HYDRATE CORES

CONSOLIDATED ROCK	DENSITY (g/cm ³)	POROSITY (%)
Berea Sandstone	2.14	19.7
Solenhofen Limestone	2.68	0.7
Austin Chalk	1.87	30.3

The samples were jacketed in Plexiglas tubing and were immersed in a constant temperature bath for 24 hours to stabilize the samples. The Solenhofen Limestone, because of low porosity, did not permit the formation of THF hydrate and was eliminated as a test sample. Electrical resistivity and sonic velocity measurements were made on the Berea Sandstone and the Austin Chalk. An order of magnitude increase was noted in electrical resistivity upon hydrate formation, and a further increase was noted as the temperature decreased. A marked increase was noted in sonic velocity from approximately 8,500 up to 16,000 ft/s upon hydrate formation. These results indicate that the sonic velocities are strongly influenced by high-porosity rocks, while low-porosity rocks are seemingly unaffected. These results also indicate that diagnostic indicators may be developed using sonic velocity logging techniques, possibly correlatable with porosity and density measurements.

Other Synthetic Hydrates: Several types of synthetic samples are needed for further research on gas hydrates: (1) a pure (containing no sediments) methane hydrate, (2) a mixed (containing sediments) methane hydrate, (3) a methane hydrate developed in a consolidated rock matrix, and (4) a hydrate derived through high pressure while keeping the temperature constant.

In addition to the THF hydrate developed in the consolidated rock matrix of Berea Sandstone and Austin Chalk, pure samples of synthetic methane hydrate have been developed using a frost base and using a water base.

A technique was developed at the University of Pittsburgh in 1983 to synthesize methane hydrates in the laboratory (Holder 1984). This technique

uses preformed frost (ice) crystals as the seed bed for forming the synthetic hydrate. A known quantity of frost is placed in a refrigerated pressure vessel at -13°F . The frost is added in portions, and is compacted to ensure a uniform void fraction. The vessel is then closed, evacuated, and pressurized with a known quantity of methane. After the frost zone is completely saturated, the temperature is raised to 274 K and maintained for 24 hours or more. After the formation of the hydrates, excess methane can be vented. This technique will be refined to develop synthetic hydrate cores that contain dispersed sediments in an unconsolidated matrix.

A methane hydrate specimen was successfully synthesized for the first time at DOE/METC from ice at 21.2°F that was pressurized to 1,000 psi with methane. Calculations show that the ice was completely converted to hydrate after 117 hours; however, the product will be analyzed to confirm if the ice was completely converted to methane hydrate. After the synthetic hydrate was removed from the reactor, it began to dissociate readily and methane was released upon exposure to the atmosphere. Pieces of hydrate were removed from the interior and exterior of the disc-shaped sample. These pieces, when ignited, burned with a characteristic methane flame. The ignition tests qualitatively indicated that conversion of ice to hydrate occurred uniformly throughout the disc. Methane hydrates synthesized by this method are thus suited for experiments to measure electrical resistivity and permittivity and sonic velocity. Such measurements are commonly made downhole during exploratory drilling for oil and gas. These measurements will be made on subsequent samples of synthetic hydrates, and will be compared with similar measurements made on natural hydrates recovered from beneath the Pacific Ocean.

Methane hydrate has also been synthesized in the gas hydrates laboratory coldroom using a new procedure. Liquid water instead of frost was used to charge the synthesis vessel. Methane was added and the conversion of water and methane to methane hydrate occurred at 35 to 37°F . Conversion of the reactants to gas hydrate reached 100 percent after 64 hours. The vessel was then cooled over 2 days to 11.2°F . When the vessel was opened, the methane hydrate was observed as aggregates of flat, fibrous crystals on the wall of the synthesis vessel. The crystals were easily removed and were stored in liquid nitrogen. This technique provides an effective and uncomplicated way of completely convert-

ing water and methane to crystals of methane hydrate. It also provides insight into how methane hydrate crystals form under conditions that approximate known marine hydrate environments.

4.2 GEOLOGICAL RESEARCH

4.2.1 Geographic Distribution

Geological research activities are focused on the mapping and characterization of geological deposits existing within the HSZ in order to determine the factors that permit or prohibit the formation of gas hydrates in the geological environment. The research activities are concentrated in two areas of the Alaskan North Slope, identified as the NRPA and the Prudhoe Bay/Kuparuk River oil fields. Some preliminary research activities are also underway in the Alaskan National Wildlife Refuge (ANWR) region of Alaska's North Slope. Research efforts are also concentrating on several regional areas in the

offshore margins of North and South America. Figure 4 shows the locations of those basins currently being investigated.

4.2.2 Basin Analysis

Determining the geology of potential hydrate deposits requires the evaluation, coordination, and analysis of data from a number of sources. Onshore and offshore work is described for (1) offshore Alaska, (2) offshore conterminous U.S., and (3) onshore Alaska.

Offshore Alaska: Gas hydrates have been inferred to be present in sediment of the Beaufort Sea, the Bering Sea, the North Pacific Ocean, and the Gulf of Alaska, based on seismic records from marine geophysical surveys.

The most extensive mapped occurrence of gas hydrates in offshore Alaska is found in sediment of the Beaufort Sea. Seismic surveys on the outermost

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FIGURE 4. GAS HYDRATE PROSPECTS IN THE WESTERN HEMISPHERE

continental shelf and continental slope north of Alaska show possible hydrate deposits that lie between 300 and 900 feet beneath the seafloor where water depths range from about 1,200 to more than 7,400 feet. The area of continental slope over which the inferred gas hydrate occurs exceeds 6,500 square miles. The total possible extent of gas hydrate may reach at least 20,000 square miles and may encompass the entire Arctic Basin where water depths are 1,800 feet or more. The seismic data of the Beaufort Sea are most strongly developed beneath bathymetric highs. These strong reflectors may be caused by the presence of free gas beneath an impermeable cap of gas hydrates.

Gas hydrate stability curves have been developed from which the depth to the base of gas hydrates or the geothermal gradient can be predicted. A geothermal gradient in sediment beneath the Beaufort Sea was indicated to be $122^{\circ} \pm 48^{\circ}\text{F/mi}$.

Marine seismic reflection data have been observed across the Bering Sea continental slope and rise near the Navarin Basin Province in water depths ranging from 1,500 to 9,000 feet. These reflectors have two possible causes. The more shallow reflectors are inferred to represent the base of a gas hydrate zone, whereas the deeper reflectors follow a diagenetic boundary. The gas hydrate reflector is often a weak reflector, and it is difficult to identify except in those areas with bathymetric relief and an undeformed sediment cover.

Gas hydrates have been postulated to occur in the deep-water parts of the Bering Sea in the abyssal Aleutian Basin, based on velocity amplitude features (VAMP's). VAMP's are acoustic anomalies showing narrow subsurface columns of concave reflection horizons, called pulldowns, associated with gently arched, high-amplitude horizons higher in the section. VAMP's typically occur in flat-lying beds at depths greater than 1,500 feet beneath a water depth of around 12,000 feet. Gas hydrates may be responsible for VAMP's by contributing to the restriction of upward-migrating gas and fluids.

Analyses of surface sediment from the Aleutian Basin show low concentrations of methane in the upper 6 feet beneath the seafloor. These low concentrations imply that gas hydrates, if present in the sediment, do not exist immediately beneath the seafloor. Geochemical sampling of sediment from the Navarin Basin Province in areas of seismically inferred gas hydrates also shows low concentrations of methane, indicating that gas hydrates are not present near the seafloor.

Evidence for gas hydrates has been noted in sediments of the North Pacific Ocean in an area located south of the Aleutian Ridge that is known as the Amlia Corridor. Seismic reflection profiles that cross the seaward flank of the Atka Basin commonly reveal a hydrate reflector at a subbottom depth near 3,000 feet. The depth of water overlying this basin is about 13,500 feet and the geothermal gradient, interpreted from the depth of the base of gas hydrate zone, is about 70 to 80°F/mi . Gassy cores from the DSDP Site 186 in the Atka Basin provide additional evidence that gas hydrates are present.

Hydrate reflectors have been observed in the Gulf of Alaska on seismic profiles of the upper continental slope of the Aleutian Trench, southeast of Kodiak Island, at water depths of 4,800 to 6,900 feet and at subbottom depths of 1,710 to 2,010 feet. A geothermal gradient of $90^{\circ} \pm 40^{\circ}\text{F/mi}$ was estimated, based on the depths of these reflectors. The geothermal gradient has also been estimated as $82^{\circ} \pm 38^{\circ}\text{F/mi}$, assuming that the reflectors represent the base of the gas hydrate zone.

Offshore Conterminous U.S.: The inner continental margin of northern California is underlain by a well-defined seismic reflector. This reflector is at subsurface depths of 540 to 930 feet and is present beneath the Klamath Plateau, located off the coast of northern California/southern Oregon in water depths of 2,400 to 3,600 feet. The reflector covers an area of at least 2,000 square miles. The water and sediment depths and pervasive nature of the reflector all indicate the base of a gas hydrate zone. A geothermal gradient of 115°F/mi was estimated for this area. This acoustically inferred gas hydrate zone is the first to be reported from the outer continental margin of the western conterminous U.S.

Six locations containing gas hydrates have been identified in the Gulf of Mexico. The hydrates have been recovered in an area approximately 155 miles southwest of New Orleans, Louisiana, that extends 105 miles in an east-west direction. Hydrate cores have been recovered from all six of these locations.

All of the hydrates have been collected along the continental slope in water depths ranging from 1,650 to 2,950 feet and are located in the northern portions of the Green Canyon and Garden Banks lease areas. One of the samples was obtained from the Orca Basin, approximately 50 miles south of the east-west line of Green Canyon/Garden Banks samples, in approximately 7,870 feet of water. The sample locations, depths, and nature of origin are defined in Table 4.

**TABLE 4. LOCATION AND DESCRIPTION OF HYDRATE SAMPLES
IN THE GULF OF MEXICO**

AREA	LOCATION	WATER DEPTH (feet)	TOP OF HYDRATE (feet)	NATURE OF ORIGIN
Orca Basin Core	26°56' N, 91°19' W	7,870	7,940	Biogenic
Garden Banks Core 387	27°36' N, 92°11' W	2,850	2,851	Biogenic
Green Canyon Core 184	27°47' N, 91°30' W	1,837	1,847	Thermogenic
Green Canyon Core 190	27°44' N, 91°13' W	1,935	1,944	Thermogenic
Green Canyon Core 204	27°45' N, 90°33' W	2,834	2,838	Thermogenic
Green Canyon Core 257	27°23' N, 90°06' W	2,952	nd*	Biogenic

*Not determined.

The Green Canyon area is a complex region on the Louisiana continental slope. The hummocky topography is caused by salt diapirs forming large mounds, basins, and troughs. Sediment thicknesses between the diapirs reach 30,000 feet, and consist of interbedded shales and sandstones. The area is very active and is unstable because of the growth of the salt diapirs, resulting in faulting, extensive slumping, and mass sediment movement.

In order to better understand the geological environment conducive to gas hydrate formation, a geological study of the Blake Outer Ridge area was undertaken. The Blake Outer Ridge is a large sedimentary ridge in the western North Atlantic Ocean. It extends more than 310 miles southeastward from the Blake Plateau, south of Cape Hatteras. It has a maximum relief of 9,510 feet, and is the result of rapid deposition of fine-grained sediments by contour-following currents upon an abyssal plain.

Prior to about 34 million years ago, sedimentation was normal in this area, with a relatively low rate of deposition on a slowly subsiding continental slope and rise. An unconformity represents the approximate configuration of the rise and slope, and the Blake Outer Ridge has been and still is being built upon this unconformity, at an anomalously high rate of deposition. The configuration of the Blake-Bahama Outer Ridge can be modeled by assuming that deposition resulted through interaction of the northerly flowing Florida current and the southerly flowing western boundary undercurrent. Consequently, much of the sediment at the Blake-Bahama

Outer Ridge was remobilized from the Blake Plateau. Once the ridge topography was developed, it was further modified by the contouring effect of the western boundary undercurrent.

The presence of gas hydrates at the Blake Outer Ridge has been demonstrated by the recovery of hydrate-bearing sediments near the crest of the ridge. The gas hydrates occurred as fine crystals dispersed in the fine-grained sediments, at a sub-bottom depth of 780 feet and a water depth of 15,090 feet. Decomposition experiments performed on a sample indicated that the gas was primarily methane, and that the origin of the sample was biogenic. Three other sites previously drilled contained gas-rich sediments; however, no gas hydrates were directly observed.

A geological analysis of the Baltimore Canyon area was initiated in 1985. The Baltimore Canyon Trough is a major sedimentary basin that underlies the Atlantic Continental Margin of North America, offshore from New York, New Jersey, Delaware, Maryland, Virginia, and North Carolina.

This western Atlantic Continental Margin is a classic passive margin, and is generally considered the type example of geologic features developed during continental rifting and subsequent ocean formation. The basement is composed of a series of fault-bounded blocks, which were attenuated to various degrees prior to the ocean development. The crustal thinning resulted in major isostatic adjustments of the fault blocks and the loading of the margin with sediment that was eroded from the

blocks themselves and from the continent lying to the west. Thus, the subsidence of the margin is a result of isostatic adjustment, thermal contraction, and sediment loading. The margin is also cut by a series of major fracture zones, principally perpendicular to the margin.

The results of the study indicate that a wide region of the continental rise southwest of the Hudson Canyon is underlain by gas hydrates, as well as portions of the slope and rise south of the Wilmington Canyon area. Estimates of the extent of the gas hydrate area, mapped by seismic profiles and reflectors are on the order of 19,000 square miles. Reflectors have been observed down to sub-bottom depths of 950 feet. Using the assumptions of 30-percent porosity for the sediments, the total pore volume available for gas hydrate formation is on the order of 142 trillion cubic feet (Tcf). The maximum potential gas-in-place is estimated to be 1,200 Tcf, assuming 90-percent saturation of the hydrate lattice, 50-percent filling of the available pore volume, and assuming sufficient gas generation from the source material.

Onshore Alaska: The first confirmation that gas hydrates occur onshore under permafrost was obtained in 1972 in the Prudhoe Bay field. In situ natural gas hydrates are now known to occur in many Arctic environments, and pressure and temperature conditions for potentially stable gas hydrates appear to be widespread in northern Alaska. Eight of 17 wells of the NPRA show evidence of gas hydrate layers in well logs (Galate and Goodman 1982). Recovered cores, drilling operations, and open-hole geophysical logs delineate a number of probable gas hydrate occurrences on the North Slope of Alaska. Recent examination of electrical logs from 125 wells on the North Slope has resulted in the identification of 102 possible gas hydrate occurrences at 32 well sites. Although most of the gas hydrates appear to be geographically restricted to the Kuparuk oil field, studies have also included the NPRA.

Logs from the 125 wells on the North Slope were evaluated, and it was determined that in order to have an intersection between the methane hydrate stability curve and a geothermal gradient, the projected gradient within the permafrost must be equal to or less than 4.32°C/330 ft (Collett May 1983). A minimum permafrost depth with this geothermal gradient would be 760 feet, and methane hydrates should not exist in North Slope sediment where the permafrost has a thickness of less than 760 feet.

Recent subsurface geochemical sampling within the HSZ in the Kuparuk oil field indicates that the composition of the free gases within these shallow horizons is more complex than previously suspected. Gas analysis indicated the presence of a significant amount of methane and heavier gases such as ethane and propane. Minor amounts of heavier gases such as propane could alter the gas hydrate structural form, leading to a more extensive hydrate stability field than occurs from a pure methane hydrate system. Conversely, lighter gases such as nitrogen would decrease the stability of a hydrate system and would reduce the thickness of the hydrate stability field. The recovered gas hydrate core from the Eileen well showed that nitrogen is present; thus, the delineated HSZ for this area is only an approximation. The actual extent of the natural gas hydrate stability field on the North Slope cannot be determined until more geochemical analyses of the gases within the hydrate horizons have been completed.

Detailed analysis of a series of open-hole geophysical well logs from the 125 wells in the Prudhoe Bay and Kuparuk oil fields suggests the existence of 102 hydrate occurrences in 32 different wells (Collett May 1983). Gas hydrates occurred in relatively porous discrete units and in many wells in multiple zones, with individual layers ranging in thickness from 7 to 92 feet. Most of the gas hydrate occurrences appear to be geographically restricted to the Kuparuk field west of Prudhoe Bay, and there appear to be between four and six laterally continuous hydrate-saturated units within the Kuparuk oil field. The gas hydrates are restricted to a series of sandstones and gravels interbedded with multiple, thick siltstone units.

The greatest potential for hydrate occurrence appears to be in the areas of known petroleum occurrences. Permafrost has existed on the North Slope for approximately 125,000 years; this may not have been a long enough time for significant quantities of hydrates to accumulate. Structural traps containing conventional reservoirs of oil with associated gas would be the most likely place for hydrates to form, when permafrost conditions and the resulting thermal gradients are imposed. The reservoirs having gas and water phases could form hydrates, and the oil and water reservoirs could form hydrates by denudation of the light hydrocarbons in the oils.

4.2.3 Resource Assessment

In 1964, the U.S.S.R. announced a natural source of gas hydrates that could supply worldwide energy demands for centuries, according to their estimates of resource-in-place. Since gas hydrates are physical combinations of gas and water where the gas molecules fit into a crystalline structure similar to that of ice, the amount of gas stored in a given volume of hydrate is much higher than when the gas occurs in gaseous form. For example, a 90-percent saturated hydrate contains 167 standard cubic feet (scf) of gas per cubic foot of hydrate.

The areal extents of hydrate deposits in several of the study areas have been estimated and thicknesses have been developed within some of these study areas. While actual thicknesses and areal extents may be questionable, a general range of the potential volume of gas-in-place has been estimated for the seven study areas indicated in Table 5.

TABLE 5. RESOURCE ESTIMATES OF HYDRATE DEPOSITS

LOCATION	GAS-IN-PLACE ESTIMATES	
	(Tcf)	
Northern Alaska	500-700	
Offshore California	5-10	
Offshore Guatemala	5-10	
Gulf of Mexico	200-2,000	
Blake-Bahama Outer Ridge	20-70	
Baltimore Canyon Area	20-40	
Offshore Maritime Canada	5-10	

In terms of energy content, gas hydrates are more comparable with heavy oil and tar sands than with unconventional gas. Unconventional gas sources contain from 1 to 12 cubic feet of gas (2,000 to 10,000 Btu) per cubic foot of reservoir, while gas hydrates contain about 50 cubic feet of gas (50,000 Btu) per cubic foot of reservoir. In comparison, conventional gas contains from 10 to 20 cubic feet of gas per cubic foot of reservoir. A heavy oil reservoir can contain about 150,000 Btu (150 cubic feet gas equivalent) per cubic foot of reservoir. After adjusting for a recovery efficiency of 30 to 40 percent, the recoverable energy of 45,000 to 60,000 Btu per cubic foot of heavy oil reservoir is similar to that of gas hydrates.

4.3 DIAGNOSTICS RESEARCH

Diagnostic research efforts are currently focused on the evaluation of both surface and subsurface geophysical techniques, as well as geochemical analysis, in order to identify features that can aid the explorationist in locating and defining the gas hydrate reservoir geometry as it exists in the geologic environment. Current studies focus on seismic reflectors, well logging techniques, and geochemical conditions within the HSZ.

4.3.1 Geophysical Analysis

Diagnostic efforts focus on the interpretation of existing logs, and are based on the implied or inferred presence of hydrate reservoirs. Anomalous behavior in the logs of known hydrate regions can be attributed to the presence of hydrates. However, to extend these findings to unknown or unexplored regions requires more definitive study and an evaluation of the geophysical and seismic characteristics of hydrate reservoirs. Surface and subsurface instruments need to be developed that can distinguish hydrates from ice or water, and that can perform down-hole measurements of reservoir temperature, pressure, porosity, and in situ stresses.

There have been strong indications of hydrate accumulations in the offshore environment during drilling and coring of certain formations. The widespread occurrence of a bottom simulating reflector (BSR) has been noted in the marine environment from seismic records obtained in widely separated areas of the world's oceans (i.e., Gulf of Oman, Black Sea, Gulf of Mexico, Bering Sea, Beaufort Sea, U.S. Atlantic Coast, and U.S. Pacific Coast). The BSR is believed to be an anomaly that is caused by a consolidated (frozen) zone in the bottom sediments, overlying an unconsolidated zone of sediments containing free gas. Analysis of the HSZ in the regions of the BSR indicates that the geothermal gradient intersects the stability curve at or near the lower boundary of the BSR. Since the sonic velocity of the hydrate-filled sediments is lower than that of unfrozen or conventional gas reservoirs, the BSR appears to indicate the base of the gas HSZ. Table 6 shows the BSR depths and areal extents of study areas in U.S. waters.

Open-hole geophysical logs also strongly suggested the presence of naturally occurring, in situ gas hydrates. The mud log indicated that a significant amount of free gas was liberated from the hydrate

**TABLE 6. BOTTOM SIMULATING REFLECTORS (BSR'S) IN
POTENTIAL GAS HYDRATE AREAS**

AREA	BSR DEPTHS (feet)	WATER DEPTHS (feet)	BSR AREAL EXTENT (square miles)
Beaufort Sea	300-900	1,200-7,400	6,562-20,072
Bering Sea	1,640	1,500-9,000	nd*
Aleutian Trench	3,000	13,500	nd
Gulf of Alaska	1,710-2,008	4,800-3,566	nd
Offshore Northern California	541-929	2,400-3,560	2,000
Blake Outer Ridge	1,476-1,870	8,200-11,480	12,352
Baltimore Canyon	820	6,562-15,093	20,458
Gulf of Mexico	100-2,625	1,312-13,124	3,088

*Not determined.

interval during drilling. Logs, such as the dual induction and the compensated sonic, indicated the presence of hydrates with anomalously high resistivities and transit times within the suspected gas hydrate zone. A recovered hydrate sample had a gas composition of 92.79-percent methane, 7.19-percent nitrogen, and minor traces of carbon dioxide, ethane, and propane.

The occurrence of hydrates identified in well log analyses indicates that the controlling characteristics for hydrate formation are localized, forming disseminated deposits with varying hydrate concentrations. Large quantities of gas hydrates do not occur as massive blanket deposits in the sediments in the HSZ. Well log analysis methods, however, cannot detect all disseminated hydrates in low-porosity sediments, and evaluation with this method is limited to detectable concentrations. Specifically, the porosities and permeabilities must be high enough to allow the flow of water and gas, and a sufficient supply of water and gas is necessary to form hydrates.

A new suite of logs, which permits the distinction between conventional reservoirs and the hydrate reservoir, must be developed. Currently, the carbon oxygen log shows promise as an analytical tool, as it can differentiate between water and hydrates. The detection of gas hydrates is possible using the sonic and electrical resistivity logs now in existence. Other tools that may be useful are the density log, carbon/oxygen log, and nuclear magnetic resonance (NMR) log. Some of these logs are relatively

new and interpretative techniques need to be developed. Some current logging tools need to be modified, and interpretative techniques for these tools need to be modified. New instrumentation is needed for other techniques, such as an optical measurement tool. Geophysical methods such as seismic surveying also appear to be effective in hydrate detection, as shown in the offshore environment by the BSR signal.

An electromagnetic survey on the North Slope to determine permafrost depths is being evaluated. Such a survey could provide insight into possible thermodynamic controls on in situ hydrates. A series of electromagnetic soundings have been made along a survey line from Reindeer Island to the main dock at Prudhoe Bay, with an extension southward of approximately 12 miles through the center of the Prudhoe Bay oil field. The generated values from this survey will be used with shallow temperature probe data to define a North Slope onshore-to-offshore transitional permafrost model. The depths to the base of the permafrost obtained from the electromagnetic survey can be compared to values obtained from onshore well log data in order to evaluate the electromagnetic system for future applications in regions without well control.

The development of more selective instruments specific to gas hydrates will permit an increasingly accurate estimation of hydrate reservoir locations. In addition, such instruments will provide more precise information on the in situ characteristics of gas hydrates and hydrate-filled sediments.

4.3.2 Geochemical Analysis

Geochemical efforts are underway in the Gulf of Mexico and in both onshore and offshore areas of Alaska. Available samples are being analyzed from recent offshore expeditions at Texas A&M University, from wells in the Prudhoe/Kuparuk areas of Alaska, and from the DSDP through the National Science Foundation.

Core recovery and in situ measuring devices need to be developed specifically for gas hydrates. Hydrate formation conditions and sedimentary stress levels within hydrate reservoirs are not well understood. Better measurement techniques would help researchers to gain this understanding. Geochemical characteristics can also be used in gas hydrate diagnostics. Recent geochemical studies in the Guatemala area indicate that salinity may be used to identify gas hydrate deposits.

Gas hydrate formation excludes the salt ions in seawater from the hydrate crystal lattice. During hydrate dissociation caused by coring and drilling, fresh water is released. Downhole chloride ion concentrations of interstitial water from hydrate-bearing core sections may decrease as the result of dilution of normal seawater dissociation of hydrate. Thus, pore water freshening determined from chlorinity data may be a reliable indicator of the presence of hydrate. Kvenvolden (1984) even speculates that the magnitude of the decrease in chlorinity is directly related to the amount of hydrate present in the interval sampled.

Chlorinity data from DSDP Sites 102, 103, 104, and 533 within the Blake-Bahama Outer Ridge area have been compiled and are shown on Figure 5 along with the approximate positions of the chlorinity minimum for each of the four sites, using the apparent minimums for Sites 103 and 104. At only two sites (102 and 533) were pore waters analyzed for the entire drilling interval; only one of the four drill holes (Site 104) terminated near the base of the HSZ. However, a downhole freshening trend is discernible in all four cases; this trend may be attributed to the presence of hydrates within the drilled intervals. Downhole chloride ion concentrations appear to reach a minimum within the HSZ. No discernible chlorinity signature was related to the hydrate occurrence at the 780-foot subbottom of Site 533. This may be because the hydrate interval cored was thin and isolated (Jenden and Gieskes 1983).

Seismic surveys within the Blake Outer Ridge area have resulted in the identification of BSR's, interpreted to be a reflection from the gas/gas-hydrate contact at the base of the HSZ. Assuming that the BSR is the base of the HSZ, the areal extent of the hydrate zone can be mapped. The areal extent identified by BSR's is approximately 20,000 square miles. The subbottom depth to the BSR for the area is approximately 1,880 feet. If one were to calculate the available pore volume for hydrate formation, assuming 30-percent porosity, the maximum pore volume would be $20,000 \text{ mi}^2 \times 1,880 \text{ ft} \times .30 = 940 \text{ Tcf}$. Combinations of the geophysical and geochemical diagnostics can provide reasonable interpretations and models of a gas hydrate reservoir.

Several chemical parameters have been identified that require further analysis:

- Whether methane generated by microbial activity is present, and whether sufficient organic matter is preserved to support the microbial activity.
- How much supersaturation of the fluid phase with gas is required for the nucleation and growth of hydrates. This might be achieved during the bubble phase.
- Whether hydrate crystallization is facilitated by the presence of structured water at clay interfaces.
- Whether the destruction of hydrates releases excess gas, which may migrate upwards and may be reincorporated into hydrates within the stability field.
- Whether anomalous zones of chlorinity, salinity, and alkalinity are related to the presence of gas hydrates.

4.4 PRODUCTION TECHNOLOGY RESEARCH

4.4.1 Production Concepts

How much gas can be produced from a hydrate reservoir depends on the effects of hydrate dissociation on formation structure, porosity, permeability, and competence. As the hydrates dissociate into gas and water, or gas and ice, the character of the reservoir may change drastically. Conventional drilling stimulation and production techniques need to be studied to see if they can be used in a hydrate reser-

FIGURE 5. CORRELATION OF PORE WATER CHLORINITY AND HYDRATE ZONES IN THE OFFSHORE U.S. EAST COAST

voir. The technological and economical aspects of various conventional production schemes need to be compared and analyzed. Unconventional concepts and techniques for gas production also need to be examined.

Unconventional recovery schemes that might be used in hydrate reservoir production include depressurization, thermal injection, solvent injection, salt fracturing, and in situ combustion. However, modifications of thermal injection schemes will be necessary, particularly during onshore drilling in permafrost. Melting of the permafrost may cause equipment instability from subsidence in the region of the injection or producing well.

Solvents such as methanol may also be injected into the hydrate reservoir to dissociate the hydrates. The solvent could be recovered at a production well and then be recycled. Using salt as a proppant will improve the effectiveness of steam or solvent injection, since salt shifts the hydrate stability curve to the left. (Figure 2 shows a methane hydrate stability curve.) In situ combustion is also a potential production method, where methane and oxygen are injected into the reservoir and are ignited. The controlled combustion of methane within the reservoir provides the energy for dissociation of the hydrate, allowing the production of the liberated gas. Use of any of these conventional methods depends on the overall energy efficiency; that is, the energy recovered must be greater than the energy expended to dissociate the hydrate. Losses to the surrounding reservoir rock can be significant.

Potential unconventional extraction techniques include the use of microwaves and electrical waves to dissociate the hydrate, depressurization of the reservoir, burial of radioactive wastes to provide thermal energy for dissociation, water jet drilling, and sea floor mining.

4.4.2 Production Modeling

Four conceptual models are currently being developed at DOE/METC: (1) a single-well thermal injection model, (2) a multi-well continuous thermal injection model, (3) a depressurization model, and (4) an in situ combustion model. A model that combines thermal injection and depressurization has also been studied, and Los Alamos National Laboratory has defined salt injection and steam injection models. DOE/METC has begun to evaluate and develop a fracture stimulation model for the production of gas hydrates.

The *Single-Well Thermal Injection* model analyzes the recovery of gas hydrates by injecting steam in a series of cycles into the reservoir surrounding a single well. The reservoir is stimulated, and the stimulation can create horizontal, vertical, or radial fractures. Then steam is injected, the well is shut-in for a soaking period, and finally, water and gas are produced. The process is then repeated as steam is injected into the increasingly larger, hydrate-free reservoir volume.

The *Multi-Well Continuous Thermal Injection* model is a multi-well recovery scheme in which steam is injected into one well, and flows through the reservoir toward a second (or more) well(s) while giving up energy. The production wells produce gas, water, or both. An extensive vertical (or horizontal) fracture is used to initiate and sustain sufficient steam injection and the production of water and gas. Heat given off by the steam dissociates the hydrates, resulting in the segregation of gas and water. The gas fills the top of the reservoir above the water well that is located in the bottom of the reservoir. Gas is produced from the upper portion of the vertical fracture.

The *Depressurization* model assumes that a horizontal fracture with a large surface area is created in the hydrate reservoir at or near the interface of a hydrate zone and the underlying sediment. The pressure is then lowered in the fracture and some of the hydrate dissociates, thereby cooling off the reservoir at the dissociation front. A thermal gradient is established, and heat flows by conduction from the overlying and underlying strata to the dissociation front.

The technical feasibility of producing gas from gas hydrates using an *In Situ Combustion* model has been evaluated. A portion of the methane from gas hydrate can be combined with injected oxygen to provide thermal energy for gas hydrate dissociation. Preliminary energy balance calculations suggest that the process will continue in a hydrate reservoir that has a porosity of 30 percent, but the process will not sustain itself initially if the porosity is 15 percent or less. However, hydrates will likely be in unconsolidated material, and the porosity of unconsolidated reservoirs is generally greater than 30 percent. Approximately 38 percent of the thermal energy in a hydrate reservoir is lost when the reservoir rock is heated to the methane combustion temperature of 177°F. Approximately 15 percent of this energy is used to increase the temperature of the water produced by methane combustion to the

reheat temperature of 177°F. A portion of the remaining heat is used to dissociate additional gas hydrates, and a portion is lost during the soak phase.

The in situ combustion, thermal injection, and depressurization concepts have been evaluated for varying geological conditions of hydrate deposition. Since hydrates occur onshore and offshore and in unconsolidated or consolidated sediments, and since hydrates form as disseminated, nodular, layered, or massive deposits, a variety of production techniques may be required to produce the hydrates. The evaluation of the three gas production concepts has yielded several by-products: (1) information on lab-scale experimentation for the recovery of gas from gas hydrates, (2) a novel concept of a line-drive moving well system for recovery of gas from gas hydrates, and (3) initial development of an analytical model that can simulate gas production from gas hydrates with the in situ combustion process.

The three production concepts are being developed into operational models and their usability is being tested. The cyclic thermal injection and depressurization models are in preliminary operational stages. A workable simulation model for hydrate production is planned that incorporates in situ combustion, thermal injection, and depressurization concepts.

4.4.3 Environmental Assessment

The environmental aspects of permafrost and subsidence are a planned part of gas hydrates research. In the complex environments where hydrate reservoirs are likely to occur, the less technically oriented issues may play a determining role in the ultimate exploration of the resource. In permafrost regions, even conventional drilling must combat the environmental, ecological, and safety barriers associated with permafrost subsidence. Storage and disposal of drilling mud for example, is a major concern in the fragile Arctic environment.

Economics issues also need to be addressed. The extraction and production of gas from hydrates will not proceed unless the resource proves to be economically attractive. Market studies dealing with production, transportation, and consumption are needed before any gas is produced from hydrate reservoirs.

4.5 RESEARCH INTEGRATION

4.5.1 Geologic Analysis System

Work efforts have continued on the development of a structured data base for gas hydrates. GAS has been developed as a part of this data base. GAS is a comprehensive package developed through a cooperative agreement between DOE/METC and the USGS, Menlo Park. It provides extensive geologic data handling capabilities. The system comprises several components, including extensive well data, graphics routines, and applications programs. Data are integrated from four data bases simultaneously. Three of GAS's basic functions include (1) Data Storage and Manipulation (Well Data Retrieval, Well Data Mapping Programs, North Slope of Alaska Data, and Drilling and Completion Data); (2) Report Generation (Geochemistry Reports, Well Data Reports, and Geologic Reports); and (3) Graphics Displays (Geochemistry Graphics, Seismic Maps, Log and Lithology Graphics, and Paleontological Data Displays).

Preliminary maps have been prepared that show the potential types of data displays using GAS as an analytical tool. These maps have been prepared for a sample area selected on the North Slope of Alaska between 148 and 153°W longitude and 60 to 70°30' N latitude. Data on permafrost depths, stratigraphic units, and porosity and permeability are being inventoried for this area, specifically for wells between 300 and 6,000 feet in depth. Once GAS is operational, detailed geologic maps will be developed that show permafrost depths and temperature and pressure gradients in order to identify potential hydrate stability zones.

4.5.2 Hydrate Data Base Development

The Hydrate Technical Data Base has been structured to conform to data sets that are compatible with GAS. A North Slope of Alaska data base has been developed that contains ten hydrate data sets. Seven of the data sets contain data derived directly from wells in the region. The other three data sets contain seismic, gravity, and outcrop information. All of the North Slope information is from the region of Alaska north of 68°N latitude. Most of the well information is from the Prudhoe Bay area and the NPRA, formerly referred to as the Naval Petroleum Reserve No. 4. The following is a description of the seven well-related data sets. The GAS dataset name is indicated in parentheses after the file name.

- *North Slope Well File (NSWF)*: contains well identification, location, casing, rock units penetrated, core, test, log, and other general information on 807 wells.
- *Porosity/Permeability File (PPI ϕ)*: contains porosity, permeability, and saturation data from 73 extensively cored wells in the NPRA.
- *Petrography File (PETR)*: contains data gathered from examinations of sandstones in thin sections from 39 wells. The mineralogy, texture, porosity, and permeability data are intended to aid in the assessment of reservoir characteristics.
- *Permafrost File (PFROST)*: contains elevations above or below mean sea level for permafrost tops and depth to permafrost bottoms. The file contains data for 70 wells.
- *Lithology File (LITHOL)*: contains unique rock types and their depth intervals for 83 wells obtained from sample and log data.
- *Paleontology File (PALEO)*: contains information indicating presence and population of foraminifera dinoflagellates, radiolaria, acritarchs, pollen, spores, and other miscellaneous fossils found in 39 wells.
- *Geochemistry File (GEOCHEM)*: contains data resulting from geochemical analyses of core and cutting samples from 68 wells.
- *Gravity File*: contains data collected between 1974 and 1980 from over 53,000 locations in the North Slope of Alaska. The data consist of line identification number, location, station elevation and number, ice and water depth, observed gravity, free air anomaly, and two Simple Bouguer Anomaly values.
- *Seismic File*: contains data for picked seismic reflections at 8,500 locations within the North Slope of Alaska. At each location, the time, depth, and velocity values are given for up to 26 defined horizons within the region.
- *Outcrop File*: contains information from 33 stratigraphic sections measured within the Nanushuk Group in the Northern Foothills. The sections were measured and described in detail; the data were gathered on strip charts, and were converted into a computer file that is designed to generate a stratigraphic column of the described section.

A listing of the 33 sections in the file identifies the sections by the American Petroleum Institute (API) number, section name, stratigraphic thickness, and rock unit at the top and base of the section.

An additional Report File contains daily drilling information for 21 wells drilled within the NPRA. The first page of information for each well contains location, date, contractor, rig, well name, classification, and total depth. Each subsequent page contains daily drilling data for the well, including standard drilling information.

5.0 RESEARCH REMAINING

Research is continuing to augment the hydrate knowledge base and enhance the understanding of the resource. Geologic research will continue, using drilling records from the DSDP and the Ocean Drilling Program, other USGS and industry records in Alaska, the offshore and geologic characterization of gas hydrates from samples generated in the laboratory, and from cores recovered from the natural environment. Laboratory experimentation on natural and synthetic gas hydrate samples will provide basic data for the development of reservoir models. Data from the analysis of onshore well logs and offshore seismic records will provide information on geological characteristics, thereby allowing further refinement of the reservoir models. The data base and reservoir simulations will be used (1) to develop feasible extraction and production models, and (2) to identify remaining data gaps in the knowledge base.

Future research activities need to focus on the diagnostics and the production mechanisms of gas from both the hydrate zone and the gas trapped below the hydrate cap. The environmental and economic concerns of hydrate production need to be evaluated for onshore and offshore regions. Field verification would provide input towards a resource assessment, and would aid in providing the proof-of-concept for gas hydrate development techniques.

The purpose of gas hydrates research is to evaluate the potential of naturally occurring gas hydrates as an energy source. The Federal role provides the coordination, integration, and synthesis of research efforts in order to establish an estimate of reserves for future use. Successful completion of these efforts

should (1) provide a well developed data base, (2) remove technological barriers preventing resource extraction, (3) influence industry activities, and (4) provide a base for commercial development of this unconventional gas resource.

6.0 ACRONYMS AND ABBREVIATIONS

API	American Petroleum Institute
ANWR	Alaskan National Wildlife Refuge
BSR	Bottom Simulating Reflector
DOE	(U.S.) Department of Energy
DSDP	Deep Sea Drilling Project
GAS	Geologic Analysis System
GEOCHEM	Geochemistry File of GAS
GRI	Gas Research Institute
HSZ	Hydrate Stability Zone
LITHOL	Lithology File of Gas
METC	Morgantown Energy Technology Center
n	Number of Water Molecules Per Guest Molecule in the Lattice Structure
NMR	Nuclear Magnetic Resonance
NPRA	National Petroleum Reserves of Alaska
NSWF	North Slope Well File of GAS
PALEO	Paleontology File of GAS
PETR	Petrography File of GAS
PFROST	Permafrost File of GAS
PPIØ	Porosity/Permeability File of GAS
R	Ratio of Molecular Diameter to Free Cavity Diameter
r	Average Center-to-Center Intermolecular Separation Unit
R&D	Research and Development
THF	Tetrahydrofuran
UGR	Unconventional Gas Recovery
USGS	U.S. Geological Survey
VAMP	Velocity Amplitude Feature

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