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Development of Alaskan Gas Hydrate Resources

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1.0 TECHNICAL PERSPECTIVE

Solid, ice-like mixtures of natural gas and water in the form of natural gas hydrates have been found immobilized in the rocks beneath the permafrost in Arctic basins, and in muds under the deep waters along the American continental margins in the North Sea and several other locations around the world. The Arctic areas of the United States may contain as much as 500 trillion SCF of natural gas in the form of gas hydrates (Lewin and Associates, 1983).

While the U.S. Arctic gas hydrate resources may have enormous potential and represent the long term future source of natural gas, the recovery of this resource from reservoir completely "frozen" with gas hydrates has not been commercialized yet. Continuing study and research is essential to develop technologies which will enable a detailed characterization and assessment of this alternative natural gas resource; development of cost effective extraction technology.

2.0 OVERALL PROJECT GOALS

The overall project objectives are outlined as follows:

1. To Gather Data and Information Relevant to Gas Hydrates in the Arctic

The specific aspects include:

- * Geology of Alaska's North Slope Region
- * Geothermal Gradient Data for Alaska's North Slope (ANS)
- * Tar Sand Deposits of Alaska's North Slope
- * Land-Sat and Other Related Remote Sensing Surveys of ANS
- * Depths, Thicknesses and the Areal Extent of Permafrost on the ANS
- * Seismic Data of ANS
- * Electromagnetic Surveys and Profiles of ANS
- * Ground Water Availability of ANS
- * Subsea Permafrost of the Beaufort Sea
- * Data and Maps of the ANS Oil and Gas Well Locations

2. To Review Gas Hydrate Literature, Current Research, State-of-the-Art Technology

The specific aspects include:

- * Compilation and Review of Gas Hydrate Phase Equilibrium Data and Predictive Models
- * Review of Gas Hydrate Recovery Models
- * Review of Gas Hydrate Properties and Compilation of Available Literature Data
- * Review of Geologic Occurrence of Gas Hydrates
- * Review of Methods for Detection of Gas Hydrates
- * Review of Potential of Gas Hydrates as an Energy Resource
- * Review of Other Gas Hydrate Literature and Current Hydrate Research

3. To Develop Contacts

To develop contacts within the petroleum industry and other agencies within the State of Alaska to obtain access to well logs, core samples, water samples and for in-situ measurement of potential gas hydrate zones and to provide DOE with all of the public information.

4. To Study Implications of Dissociation of In-Situ Gas Hydrate Deposits

The following aspects are addressed:

- * Implications Related to Drilling and Production from Hydrates
- * Development of Thermal Model to Predict, the Degree of Dissociation of Gas Hydrates During Drilling
- * Development of Guidelines for Drilling in Presence of Hydrates
- * Effect of Dissociation of Gas Hydrates on Subsidence
- * Mechanical Properties of In-Situ Gas Hydrates

5. To Conduct Experimental and Theoretical Modelling Work for the Development of Techniques for Recovery of Natural Gas from Gas Hydrates

A. The experimental work on study of hydrate cores address the following:

- * Formation of Gas Hydrates Within the Porous, Unconsolidated Cores and Measurement of Hydrate Formation Rates and Study of Kinetics
- * Measurement of Permeability of Cores During Hydrate Formation, as a function of hydrate saturation.
- * Dissociation of Hydrates Under Various Conditions (such as, depressurization, hot brine and steam injection and measurement of gas production rates)
- * Study Hydrate Dissociation Mechanism, Heat Transfer Mechanism and Convection Effects Under Above Conditions

B. The hydrate recovery modelling efforts include:

- * Development of a fundamental hydrate dissociation model which considers unsteady state heat transfer to hydrates in r-z directions. This will be a

finite difference simulator and will include both heat conduction and convection effects.

- * Application of the model to brine, hot water, steam injection and depressurization methods. Experimental data will serve as the basis of our theoretical model.

6. To Conduct Economic Analysis of Gas Hydrate Production

The analysis will consider various hydrate recovery methods and compare relative costs. The results of our hydrate recovery models will serve as the basic data for the economic analysis. Also, the various options of natural gas utilization will be evaluated.

7. To Conduct Experimental Study of Hydrate Formation in the Presence of Heavy Oil

In reservoirs where gas hydrates coexist with heavy oil or tar sands it is possible that gas hydrates might have affected the properties of these heavy oils and also may affect the performance of thermal recovery methods. To develop better understanding of hydrate-heavy oil relationship the research is devoted to the following:

- * Study hydrate formation from light hydrocarbon gases and West Sak and Prudhoe Bay crudes
- * Measure equilibrium hydrate forming conditions
- * Study effect of hydrate formation on the oil properties (such as, bubble point pressure, density and viscosity)

3.0 WORK PERFORMED DURING FIRST YEAR

- Section I:** Alaskan Arctic North Slope Data Gathering
- Section II:** Review of Gas Hydrate Literature, Current Research, State-of-the Art Technology
- Section III:** Hydrate Dissociation Modelling and Implications of Hydrate Dissociation During Drilling in Arctic Offshore and Onshore Environments
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SECTION I

ALASKAN ARCTIC NORTH SLOPE DATA GATHERING

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1. Alaskan Arctic North Slope Data Gathering

During the past year, we have conducted a thorough literature search to gather available information on geology of ANS; geothermal gradient data for ANS; Land-Sat and other related remote sensing surveys; depths, thicknesses and the areal extent of permafrost on the ANS, seismic data, electromagnetic surveys and profiles of ANS; ground water availability, maps and data of ANS oil and gas well locations. A complete bibliography of all the published information has been prepared. Review reports for some of these areas are given in this section. We will submit review reports for other areas later. A set of documents have been delivered in the past to DOE-METC.

In addition to the published information, we have also focussed our attention on acquiring digitized well log data for wells located on the ANS and offshore Prudhoe Bay areas. We have received digitized well log data on magnetic tapes from Alaska Oil and Gas Conservation Commission. The well log data will include wells from the following areas of ANS:

1. West Sak Sands in the Kuparuk River Unit (25 wells)
2. Ugnu Sands in the Kuparuk River Unit (10 wells)
3. Kuparuk Formation in the Kuparuk River Unit (250 wells)
4. Prudhoe Bay Unit (200 wells)
5. Offshore Prudhoe Bay Unit (not yet received)

For well log analysis, we have received software packages LOGCALC and LOGCALCII from Scientific Software Intercomp. These software packages have been installed and tested. Histograms, crossplots, three-dimensional plots can be generated using these interactive software packages to aid quick well log analysis.

2. Geology of Alaska's North Slope Region

Alaskan North Slope region is subdivided tectonically into three major east-west trending elements. These elements are the Barrow Arch, Colville Trough, and Brooks

Orogen. The Barrow Arch is a subsurface broad regional structure. The axis of this arch follows the Beaufort Coast from the foothills of the Brooks Range to Point Barrow and continues onto the Chuckchi Sea. The arch developed during Late Jurassic or Early Cretaceous time on the northern province of the Arctic platform. Consequently, southward-sloping platform south of the arch and a northward-sloping continental margin north of the arch evolved Cretaceous and Tertiary sedimentation north of the arch prograded the Beaufort continental terrace north from the arch across the presently formed continental margin.

The earliest known tectonic feature on the North Slope region is the east-west oriented Colville Geosyncline. Between Cambrian and Devonian times, the geosyncline was filled with miogeosyncline of rocks, both ev- and miogeosyncline facies, which are metamorphosed. Sometimes during the Devonian time the region was uplifted and a broad stable Arctic platform extended along Northern Alaska. Marine sedimentation continued for late Devonian or Early Mississippian through Early Cretaceous times and created the second sequence of rocks. Clastic and carbonate sediments derived from a northern source area were deposited on the platform. Near Prudhoe Bay these rocks contain giant oil and gas accumulations. At the close of the Jurassic or the beginning of Cretaceous time, intense tectonic activity compressed the southern part of the platform and thrust Paleozoic to Cretaceous rocks northward onto the central part of the platform. The compression resulted in the uplifting of the Brooks Range - Herald Arch, which subsequently supplied sediments detritus for the third sequence. Cretaceous sedimentary rocks of the Colville Geosyncline underlie most of the Northern Chuckchi Shelf and North Slope.

The major filling of the Colville Geosyncline occurred during the Cretaceous. The continued uplift in the Brooks Range intermittently supplied detritus northward during the Tertiary. The area was exposed and submerged under the sea repeatedly. From the Middle Eocene until Middle Pliocene time the region was above sea level. The area may

have submerged briefly as a result of deposition of the fourth sequence. During the Tertiary a stream-sculptured topography similar to that observed today probably developed on the North Slope region.

At the beginning of the Pleistocene epoch crustal warping resulted in marine transgression and the final sequence of sediments was deposited on the North Slope region. The sediment deposited during the Pleistocene have covered the Tertiary topography and formed a monotonously flat platform.

The Pleistocene epoch also connotes a repeated ice cover during glacial stages and the wanning of glaciers during interglacial stages. Each glacial cycle was followed by changes of sea level in Northern Alaska. The brightest sea level attained during the interglacial stage is estimated at about 30M higher than present sea level. During intense glacial marine intervals the sea level fell about 100M below the present strandline.

On the North Slope the unconsolidated Quaternary sediments overlies Tertiary or Cretaceous sediments. The Quaternary sediments are mostly fine-grained sand and silt and occasionally clay and gravel, which are product of frosting and aeolian deposition. The entire region is underlain by permafrost, which acts as a cement for these sediments. However, annual freezing and thawing in the upper layer forms loose sediments, which are modified by alluvial, Lacustrine, and aeolian reworking and tundra soil development.

The Brooks Range Orogen is dominated by thrust faults, and the subsurface geology in the area is not well known. Northern parts of the Brooks Range, the Foothill Fold Belt, consists of shallow folds with complex axial shale cores while southern zone comprising similar complex folds and thrust faults. Several structures in the northern part of the Foothills Fold Belt are hydrocarbon bearing and may have contributed to formation of gas hydrates.

The potential reservoir beds in the North Slope region of pre-Tertiary age in

ascending order are:

1. Mississippian-Pennsylvanian clastic facies of the Lisburne Group;
2. Mississippian "Dolomite Unit" of the Alaph Limestone;
3. Pennsylvanian-Perian Wahoo Limestone;
4. Permian Ikiakpaurak member of the Echooka Formation;
5. Triassic "Ivishak Sandstone";
6. Triassic Sag River Sandstone;
7. Early Jurassic "Barrow Sandstone";
8. Late Jurassic "Simpson Sandstone";
9. Jurassic-Neocomian Kuigak Formation includes potential reservoirs "Peard Sandstone", Neocomian "Kealok Anomaly"; and
10. Cretaceous rocks include "Pebble Shale" sandstone, "Walakpa Sandstone", Basal Torok", and marine and nonmarine sandstones of the Nanushuk Group.

3. Groundwater Availability of ANS

Most of the North Slope region is underlain by as much as 550m thick layer of perenial frozen material called permafrost. Between the ground surface and the upper permafrost is a shallow layer of soil that thaws to a maximum depth of 0.5m during the brief summer and refreezes during late fall. This soil accumulates water from rain, snow and ice melt but deeper infiltration of water is prevented by the permafrost. The presence of permafrost in the North Slope region provides unlimited supply of surface water during summer, the lack of subsurface drainage severely limits the availability during other seasons.

North Slope region is covered by numerous large and small lakes and marshes and drained by numerous rivers and streams. Arctic lakes can be divided into two categories: 1) glacial lakes and, 2) thaw lakes. Glacial lakes are formed in the foothills and upper reaches of the Brooks Range close to the source of the glacier. These are few

in numbers and are mostly located in the southern regions.

Thaw lakes, quite common and numerous are formed by the pooling of melted snow and ice in shallow depressions, augmented during summer by the thaw from underlying permafrost. Summer thaw over long period widens and deepens the lake.

During winter water supply can be drawn from unfrozen alluvium located beneath deeper lakes and deep meander pools along the channels of the major rivers, commonly known as thaw-bulb. Near the coast thaw-bulb may contain brackish and saline water, inland the water quality is generally good. The year round availability of potable water from thaw-bulb have been evaluated, however, overall quantity and reliability of the fresh water supply in the North Slope region has not been fully explored. Black (1955) reported large quantities of ground water on the Arctic Slope in deep lakes, major perennial streams, and in hot spring areas. He noted that permafrost surface is significantly lower or even absent under major rivers which flow throughout winter and have flood plains extending over hundreds of meters. The thickness of alluvium containing sandy gravel of varying thickness, generally between few meters and 10's meters.

The alluvium aquifers underlying river generally have better quality water and greater storage potential than those underlying lakes because rivers recharge their aquifers during flow period. Lakes on the otherhand at surface freeze to a depth of 2-3 meter and thus transfer impurities to the underlying unfrozen bottom water.

The winter storage capacity of some thaw-bulb can be increased by pumping freshwater during thaw period. The storage will depend on the extent of the reservoir, rock type and flow characteristic including porosity, permeability and geothermal gradient.

4. Geothermal Gradient Data for Alaska's North Slope (ANS)

The northern part of the North Slope is mostly covered by thaw lakes and ponds.

The area is also drained by numerous rivers and their tributaries. The remainder of the areas have a thin cover of unconsolidated thin veneer of sediments with or without vegetation cover typical of Arctic tundra. Beneath these surface geomorphic features is a thick layer of permafrost. The nature of the permafrost is dependent on the lithology and the texture of the rock.

At shallow depths the geothermal gradient in the Arctic is influenced primarily by the following:

1. Actual temperature of the ground surface
2. Presence of surface water, i.e. thawed lakes, ponds and river beds
3. Presence of tundra and their vegetation cover
4. Texture and lithology of the substrate

The thickness of the underlying permafrost is to some extent dependent on the geothermal gradient, therefore, the depth of the permafrost in the Arctic varies according to the prevailing surface conditions.

During World War II the increased construction of roads and buildings in the Arctic necessitated a need for the study of characteristics and behavior of perennial frozen soil and ground. Thus, a great interest was evolved in measurements of the geothermal gradients in the Arctic. Later activities prior to and subsequent to the development of the vast fossil energy and mineral resources further intensified the investigation and measurement of the geothermal gradients throughout Alaska.

The early investigations and measurements of the geothermal gradients in the Arctic were conducted by MacCarthy (1952). Measurements near Barrow indicated that the seasonal surface variations in temperature could lower the subsurface temperatures to a maximum of -10°C . He further noticed that the 0°C isotherm varied between the depths 670 and 1,300 feet. In general, increasing in depth with increasing distance from the nearest large body of water. The depth of 0°C isotherm also defines the depth of the permafrost in this region.

Brewer (1958) published thermal data collected over a period of six years. Most importantly he identified the problems related to the temperature and distribution of permafrost in the Arctic. He confirmed earlier observations by MacCarthy that the lowest subsurface temperature reached to -10.6°C and effect of seasonal variations was limited to depth varying between 70 and 100 feet. The variations in shallow thermal gradients due to seasonal variations depended on the surface temperature, snow cover, soil moisture content and other physical properties.

The investigations of Brewer (1958) also revealed the Arctic lakes with diameter of approximately one-half mile or more and with depth of seven feet or more remained unfrozen at the bottom during winters.

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SECTION II

REVIEW OF GAS HYDRATE LITERATURE, CURRENT RESEARCH AND STATE-OF-THE-ART TECHNOLOGY

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ABSTRACT

Natural gas hydrates occurring beneath permafrost regions of the world, are gaining increasing importance in view of their enormous potential as a source of natural gas. The review evaluates the present state-of-the-art in gas hydrate literature. Various aspects of hydrate-related studies including occurrence, detection, kinetics, thermodynamics, and phase equilibrium are discussed. Finally, an attempt has been made to point out the inadequacies in areas of practical importance and recommendations for future work are outlined.

SCOPE

Solid ice-like mixtures of natural gas and water in the form of natural gas hydrates have been found immobilized in the rocks beneath the permafrost in Arctic basins and in muds under the deep water along the American continental margins, in the North Sea and several other locations around the world. It is estimated that the arctic areas of the United States may contain as much as 500 trillion SCF of natural gas in the form of gas hydrates (Lewin and Associates, 1983). While the U.S. Arctic gas hydrate resources may have enormous potential and represent long term future source of natural gas, the recovery of this resource from reservoir "frozen" with gas hydrates has not been commercialized yet. Continuing study and research is essential to develop technologies which will enable a detailed characterization and assessment of this alternative natural gas resource, so that development of cost effective extraction technology. This study presents a state-of-the-art review of the various aspects related to gas hydrates. Reviews on gas hydrates have been published earlier by Byk and Fomina (1968) and Makogen (1981). Since then, many articles have been published on different aspects of gas hydrates. An attempt has been made in this review to provide a more complete and up-to-date information of gas hydrate literature.

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1. INTRODUCTION

In regions, such as northern Alaska, where low temperatures persist far below the earth's surface, natural gases combine with water to form solids known as natural gas hydrates. Hydrate deposits are also found (Kvenvolden and McMenamin, 1980) in other regions of the world where conditions are thermodynamically favorable for their existence. Gas hydrates are nonstoichiometric, crystalline, ice-like solids formed due to encagement of gas molecules in the interstices of hydrogen bonded water lattices and have a composition of approximately 85 mole % water and 15 mole % of natural gas. They contain approximately 170-180 SCF of natural gas per cubic foot of hydrate and hence represent an attractive source of gas, provided that the gas can be economically recovered. Because of the relatively immobile and impermeable nature of the gas hydrates, they have to be dissociated to gas and water in order to produce natural gas from hydrate reservoirs.

Gas hydrates represent a concentrated form of natural gas and thus an attractive potential energy resource for the future. Enormous quantities of natural gas is estimated to occur in the world in the form of gas hydrates, though the estimated values vary widely ($1.4 \times 10^{13} \text{ m}^3$ to $7.6 \times 10^{18} \text{ m}^3$). (Meyer, 1979, Dobrynin, et al, 1979, McIver, 1979). Because of this potential resource, the production of natural gas from these naturally occurring hydrate zones and the problems associated with the production are becoming increasingly important. The possibility of production of natural gas from the hydrate zones has been proposed and preliminary work on modelling the production techniques has been done. There, however, remains a vast amount of information regarding the in situ nature of hydrates, their physical, kinetic and transport properties, that is unknown.

2. NATURE OF GAS HYDRATES:

Gas hydrates are crystalline, ice-like solids wherein the gas molecules are encaged in the interstices of the hydrogen bonded water lattices. The first published study of hydrates of gases goes back to 1810, when the English chemist, Sir Humphrey Davy, formed chlorine hydrates in his laboratory (Faraday, 1823). These studies indicated that hydrates are non stoichiometric compounds and the number of gas molecules per water molecule in the hydrate phase depend upon the conditions under which they were formed. Much of the early work in the late nineteenth century and the start of the twentieth century, on hydrates of methane, ethane, carbon-di-oxide by Faraday, Villard, deForcrand and others has been reviewed by Schroeder (1927).

The study of gas hydrates at the beginning of the twentieth century did not have any direct industrial application until the beginning of the 1930's when Hammerschmidt (1934) first reported that the plugging of natural gas pipelines was caused by hydrates. With the rapid development of gas-producing industries, subsequently, efforts were made to study hydrate forming conditions of different gases and to develop methods of preventing their formation and accumulation in gas pipelines and in wells drilled for gas production.

During the last half century, numerous experimental and theoretical studies have been carried out on measurement of pressure, temperature, and composition conditions for hydrate formation. Interest in gas hydrate research has been renewed, primarily due to the recent discovery of in situ natural gas hydrates in cold regions, such as Alaska, Canada's Northwest Territory, and in deep ocean sediments. (Stoll et al, 1971; Hand et al, 1974; Holder et al, 1976; Holder et al, 1980; Godbole et al, 1986).

3. STRUCTURE OF HYDRATES

Gas hydrates are nonstoichiometric crystalline compounds wherein the gas molecules are encaged in the interstices of the hydrogen bonded water lattices. They belong to a class of inclusion compounds called clathrates (Brown, 1962) which are nothing but chemical compounds wherein one component fits into a cavity in another component without any chemical bonding between them. In case of gas hydrates, the interaction between gas and water molecules is purely physical in nature and as such, the gas molecules are not part of the lattice framework. The gas provides stability to the hydrate phase, since, in absence of gas, no water lattice is formed.

The first attempt to investigate the structure of hydrates was made by Nikitin (1936) who suggested that gas hydrates are nonstoichiometric inclusion compounds, called "clathrates," made up of a metastable "host" crystal lattice of water molecules within which the "guest" gas molecules are held by van der waal forces. Claussen (1951), Pauling and Marshal (1952), and von Stackelberg and Muller (1954) employed x-ray diffraction techniques to study the structure of hydrates and showed that gas hydrates crystallise in either of the two structures called I and II. The water molecules forming the crystal lattice interact among each other through hydrogen bonds whereas they interact with the "guest" gas molecules through weak van der waal forces. The crystalline structure formed by water lattice is composed of cavities of different sizes, and for producing a stable hydrate, only one-third of the cavity has to be occupied by gas molecules.

Structure I unit cell is made up of 46 water molecules, with 2 small and 6 large cavities of 5.1°A and 5.8°A average free diameter respectively whereas structure II consists of 136 water molecules, with 16 small and 8 large cavities of 5°A and 6.7°A average free diameter respectively. The small cavities of structure I are regular pentagonal tetrahedra whereas the tetrakaidecahedral large cavities consists of

twelve pentagonal sides and two opposite hexagonal sides and are surrounded by twenty four water molecules. The cavity sizes are more equal in structure II, which is formed only when the "guest" gas molecules are too large to fit in cavities of structure I. Thus, e.g., propane, which has an average free diameter greater than 5.8°A, does not form structure I hydrate and can only form structure II hydrate. The smaller cavities of structure II are pentagonal dodecahedra and are slightly deformed with a mean free diameter of 5°A. On the other hand, the larger cavities of structure II are nearly spherical and are hexadecahedral. Table 1 gives the hydrate lattice properties of both the structures. Figures 1 and 2 give molecular arrangement of structures I and II.

Whether structure I or structure II hydrate is formed depends upon gas composition, molecular size and temperature of the system. In general, biogenic gases form structure I, due to smaller molecules, whereas thermogenic gases usually form structure II, with molecules larger than ethane. A hydrate is formed when the lattice has been occupied by sufficient number of molecules to result in a stable structure. The hydrate number is defined as the ratio of number of water molecules to number of gas molecules in the hydrate phase. Different values of n are possible due to the presence of unoccupied cavities at thermodynamic equilibrium. The minimum value of n for structure I is 5.75 when all the cavities are occupied and 7.66 when only the large cavities are occupied. The corresponding values for structure II are 5.67 and 17 respectively. Thus, isobutane, which can only fit into the larger cavities of structure II, should have hydrate number greater than or equal to 17. Table 2 gives the hydrate numbers for different gases.

As pointed above, the hydrate crystals can be stabilized even if the gas molecules partially occupy the available cavities in structure I or II. However, small molecules like methane cannot stabilize structure II and even structure I cannot be formed by pure hydrogen. This is because the energy of stabilization results from

van der Waal type forces, which are a function of the polarizability of molecules, and hence small molecules interact weakly with the lattice. Also, as these forces are proportional to $(1/\gamma^6)$, where γ is the average separation between the guest and lattice walls, the empty water lattice cannot be sufficiently stabilized by small molecules in large cavities of structure I and II. However, Barrer and Ruzicka (1962) showed that in presence of other hydrate formers capable of stabilizing the structures, it is possible for methane and even hydrogen molecules to occupy the smaller cavities of structure II.

In addition, Barrer and Edge (1967) and Ceccotti (1966) suggested that, apart from structures I and II, hydrates can also form other structures. Allen (1963) has substantiated this claim by showing that bromine hydrate can have a different structure with 172 water molecules and containing 20 cavities per hydrate crystal.

FIGURE 1: STRUCTURE I HYDRATE REPRESENTATION
(AFTER KAMATH, (1982))

**FIGURE 2: STRUCTURE II HYDRATE REPRESENTATION
(AFTER MAKOGEN)**

TABLE 1: PROPERTIES OF HYDRATE LATTICE**(After Kamath (1984))**

	Small Cavities	Large Cavities	Small Cavities	Large Cavities
Cavities per Unit Cell	2	6	16	8
Cavity Radius, °A	3.95	4.30	3.91	4.73
Co-ordination Number	20	24	20	28
Cavities Per Molecule	1/23	3/23	2/17	1/17

	Structure I	Structure II
1) Number of Water Molecules per Unit Cell	46	136
2) Typical Examples	CH ₄ , C ₂ H ₆ , Ar, Kr	C ₃ H ₈ , C ₃ H ₆ , i-butane, cyclo-propane

TABLE 2: HYDRATE NUMBERS FOR DIFFERENT GASES

Gas	Hydrate No. Experimental	Hydrate No. Theoretical	Reference
1) Methane	6.0		de Forcrand (1902)
	6.0		Hammerschmidt (1934)
	7.0	5.75	Roberts et al (1940)
	5.8-6.3		Kobayashi et al (1976)
	6.15		Kamath (1984)
2) Ethane	7.0		de Forcrand (1902)
	6.0		Hammerschmidt (1934)
	7.0		Roberts et al (1940)
	8.3	7.66	Deaton and Frost (1946)
	7.9-8.5		Kobayashi et al (1976)
	8.0		Kamath (1984)
3) Propane	7.0		Hammerschmidt (1934)
	18.0		Deaton and Frost (1946)
	6.0	17	Miller and Strong (1969)
	19.6-19.8		Ceccotti (1966)
	18.0		Kamath (1984)
4) i-butane	18		Schneider and Farar (1968)
	17.5	17	Rouher and Barduhn (1969)
	15-17		Godbole (1981)
5) Carbon Dioxide	6.0		Villard (1888)
	6.0	7.66	de Forcrand (1902)
	7.0		Deaton and Frost (1946)
	7.2		Kamath (1984)

4. OCCURRENCE OF HYDRATES

The widespread existence of in-situ gas hydrates in nature and their potential as an alternate resource of energy and an attractive resource of natural gas in the future has rekindled interest in gas hydrates in the petroleum industry and among researchers.

One of the earliest discoveries of in situ gas hydrates was in the mid-1960's when huge deposits of natural gas hydrates were found to occur in sediments below permafrost in Siberia in USSR. (Cherski and Makogen, 1970). Subsequently, significant quantities of naturally occurring hydrates on land have been discovered primarily in permafrost regions of the earth where low temperatures are favorable for hydrate production. Some of the regions of best potential where in-situ natural gas hydrates have been detected include the North Slope of Alaska, the McKenzie Delta of Canada, and the Western Siberian Basins of U.S.S.R., including Messoyakha Field. Figure 3 shows the potential regions of hydrate existence on the U.S. land and waters.

Onshore Hydrate Occurrences:

Gas Hydrates in the Arctic

As mentioned before, the presence of naturally occurring gas hydrates has been established in the Arctic areas of Alaska, Canada, and USSR in the subsurface permafrost zones of hydrate stability. More than 23% of the earth's land mass is covered by permafrost (permanently frozen ground) and is mainly confined to Alaska (75% of the total area), Canada (63%), USSR (47%), polar regions of Scandinavia, Greenland and Antartica (Handbook of Gas Hydrates, 1983).

Katz (1972) suggested that natural gas dissolved in crude oil could form hydrates with water phase in absence of gas phase. The sandstone reservoir of the Messoyokha field in the Soviet Union is the largest known onshore field where gas

**FIGURE 3: POTENTIAL REGIONS OF HYDRATE OCCURRENCE
IN U.S. LAND AND WATERS**

hydrates occur at a depth of 800 ft. and the reserves are estimated to be 1 billion cubic metres. In Prudhoe Bay, Alaska, hydrates can exist to depths even beyond 1200m, since the depth of permafrost itself is 700m. (Katz 1971, 1972). In fact, a crude oil was found at 1200m denuded of its lighter paraffinic components which might be explained by formation of hydrates.

Natural Gas Hydrates in the Alaskan Arctic

The interest in gas hydrates in the Alaskan Arctic was first stimulated by the discovery of huge oil and natural gas resources on the North Slope of Alaska. Katz (1971) indicated that gas hydrates can be stable up to depths of 1,200 meters on the North Slope of Alaska. On March 15, 1972, ARCO and EXXON provided the first confirmed evidence of the presence of gas hydrates in Alaska when they recovered gas hydrate core samples in pressurized core samples at several depths between 577 and 776 meters from the Northwest Eileen #2 well in the Prudhoe Bay field (Kvenvolden et al, 1980). Collett (1983) and Collett and Economides (1983) examined one hundred and twenty-five wells in the North Slope of Alaska and identified one hundred and two definite hydrate occurrences in thirty-two different wells. Godbole and Economides (1985) examined thirty-four wells in Alaska and indicated that in fourteen wells there is a possibility of hydrate occurrence. Kamath et al (1986) examined forty-six wells and showed that in ten wells gas hydrate deposits may be found.

According to Collett et al (1984), the estimated amount of natural gas trapped within gas hydrates in the Kupurak field is about 5.3×10^{10} ft³ per square mile (579×10^6 m³ per square kilometer). They used the Pickett cross plotting technique along with corrected neutron porosity and sonic porosity values to determine depth, thickness, porosity and saturation of in-situ gas hydrates. Recently, Mathews (1986) described the logging characteristics of gas hydrates in the Northwest Eileen Well

#2 and estimated the amount of natural gas trapped within hydrates to be about 1.75×10^{10} - 3.77×10^{10} ft³ per square mile (192×10^6 - 412×10^6 per square kilometer).

Offshore Hydrate Occurences :

As far as offshore areas are concerned, hydrates have been found to occur naturally mainly in the margins of the outer continental shelf, and have been detected by drilling and seismic profiling of depths of more than 450m. Stoll et al (1971) suggested that gases coming out from ocean sediments cores must be due to hydrate dissociation to gas at atmospheric pressure. Some of the offshore areas where hydrates have been found include the Beaufort Sea shelf, the Blake Bahama outer ridge on the east coast of United States, the Mid-American Trench, the west coast of Gautemala, the Gulf of Mexico, and Pacific Ocean off West U.S. coast (Halleck et al, 1982).

The presence of hydrates in the Blake Bahama outer ridge was further confirmed when the Glomar Challenger encountered marine sediments of high gas content, which showed high seismic velocities (Mollister et al, 1972) and anomaloussonic reflectors. Such a reflector, called the Bottom Simulating Reflector, was first noted Blake Bahama Outer ridge of the North Atlantic (Marks et al, 1970, Ewing and Hollister, 1972) and were subsequently also found in the North Pacific (Scholl and Creager, 1973). Table 3 gives a summary of the occurrence of gas hydrates in the world.

Estimated Reserves of Hydrates

It has been estimated that the in situ hydrate resources of U.S. may vary from 1 to 25,000 TCF for onshore deposits and from 2700 to 6,700,000 TCF for offshore deposits (McIver 1974, Meyer 1976).

Table 4 gives the estimated reserves of gas in the form of hydrates, both U.S. and worldwide. These figures for estimation of reserves of gas vary widely due to lack of sufficient data.

TABLE 3: SUMMARY OF GAS HYDRATE OCCURRENCES IN THE WORLD

Region	Reference
1) a) North Slope, Alaska b) Norton Sound, Alaska	Jamison et al (1980) Godbole et al (1987) Kvenvolden et al (1980)
2) Messoyakha Gas Field, USSR	Sapir et al (1973) Makogen (1965)
3) Beaufort Sea	Stewart et al (1983) Weaver et al (1982)
4) McKenzie Delta	Bily and Dick (1976)
5) Arctic Islands	Stuart-Smith et al (1976) Franklin (1981) Trofmuk (1977)
6) Middle American Trench	Brooks et al (1983) Hesse et al
7) Bering Sea	Cooper (1979)
8) Northern Canada	Davidson (1978)
9) Northern California Continental Margin	Field and Kvenvolden (1985)
10) Offshore Region of Guatemala	Geotimes (1982)
11) Southeast U.S.	Dillon (1980)
12) Cormorant South Subsea Oil Well	deBoer (1983)
13) a) Volcanic occurrences b) Marine sediments	Gaffney (1981) Kaplan (1974) Milton (1976)

TABLE 4: ESTIMATED RESERVES OF GAS IN HYDRATE FORM

	World On-shore	World Off-shore	U.S. On-shore	U.S. Off-shore
Dobyrynin (1979)	$2.8 \times 10^{16} \text{m}^3$	7.6×10^{18}	$7.1 \times 10^{16} \text{m}^3$	$1.9 \times 10^{17} \text{m}^3$
Meyer (1979)	$1.4 \times 10^{13} \text{m}^3$	---	$3.1 \times 10^{11} \text{m}^3$	---
Mclver (1979)	---	$3.1 \times 10^{15} \text{m}^3$	---	7.6×10^{13}
Trofimuk (1977)				

5. KINETICS OF HYDRATE FORMATION

Although several studies have been made, since the beginning of the present century to measure temperature and pressure conditions at which formation of gas hydrates begins, there has been little effort on the part of investigators to study kinetics and mechanism of hydrate formation. Thus, since the gas-water or gas-ice interfacial surface area could not be characterized satisfactorily, the specific hydrate formation rate could not be measured. Also the heat evolved due to the exothermic nature of hydrate formation at the interface, imposed additional limitations.

Thus the kinetic studies of gas hydrates can be classified into two main categories:

- a. Hydrate Formation from Water; and
- b. Hydrate Formation from Ice Crystals.

a. Hydrate Formation from Water

The first attempt to study the steady state kinetics of gas hydrate formation from water was done by Knox et al (1961), who investigated the kinetics of propane hydrate formation in a bench scale water desalination unit. They combined liquefied propane (which forms structure II) with artificial water in a 10 gallon CSTR operating at 47 psig and 35°F. Their study indicated that with increase in stirrer speed and thermal driving force, the rate of nucleation and hydrate growth increases, resulting in higher yield but produces smaller crystals. Hence, while separating the hydrate crystals from the brine solution, it is difficult to completely remove the entrapped water molecules within the solid hydrate mass.

In 1965, Pinder studied the kinetics of formation of tetrahydrofuran (THF) hydrate (structure II) at -0.5°C in a stirred batch reactor from various THF-water mixtures and employed refractive index measurements to monitor concentration

changes in the solution. In this case, since THF is water soluble, the question of a gas-liquid or liquid-liquid interface did not arise. It was found that the rate is directly proportional to concentration driving force and increases with stirrer speed. It was proposed that diffusion of reactant species between hydrogen-bonded, THF-water association complexes might be a plausible explanation of the mechanism of hydrate formation.

The majority of the studies on hydrate formation have employed dynamic conditions, where the gas-water contact surface is created by techniques like mixing, bubbling of gas through water, mechanical agitation, etc. and which results in the formation of an amorphous mass. In contrast to this, Makagon et al (1981) have studied the nucleation and growth kinetics of hydrates of natural gas under isothermal quiescent conditions. It was found that the first step in the hydrate formation process is nucleation of hydrate crystals and it invariably occurred on an interface (e.g., gas-liquid, liquid-liquid, or solid-liquid). Thus the metal walls of the experimental setup can adsorb gas molecules either from the gas phase or in solution, providing good nucleation sites. Usually hydrate nuclei are formed on the gas-water interface. In presence of crystallization nuclei, initially the crystals grow at high rates till they cover the entire surface of gas-water contact (surface-film hydrate). Subsequently, the growth of hydrate crystals takes place within gas, water or ice phases by volume diffusion mechanism, and is limited by the rate at which the hydrate forming species (probably water) diffuses to the hydrate crystal growth surface. However, the exact mechanism of hydrate formation is not yet clearly understood.

The most important factors that affect the rate of hydrate formation are the composition of parent gas, the thermodynamic conditions, and the type of crystallization. The first step in hydrate formation is the formation of crystallization nuclei on the free water surface, and is followed by the diffusion of gas from the

gas stream either to the hydrate formation surface or through the hydrate formed on the surface of gas-water contact. The size of hydrate film formed in time T depends upon the rate of formation of nuclei I and the radial growth rate of the surface film hydrate V_T

$$F = \pi V_T^2 I \tau \dots\dots\dots (1)$$

The water diffusion rate M_W through the hydrate film of uniform thickness h and with surface F is given by

$$M_W = D_W \frac{P \Delta f \rho_w}{h} \dots\dots\dots (2)$$

where

- D_W = diffusivity of water through the hydrate film.
- ρ_w = water density in the hydrate phase.
- Δf = difference in volatility of water between water (ice) and hydrate phases.

The increase in hydrate film thickness with conversion of water or ice hydrate is given by

$$h = \left(\frac{2 D_W \Delta f}{h} \right)^{0.5} \tau \dots\dots\dots (3)$$

where

- n = hydrate number.
- τ = hydrate growth time.

For experimentally obtained diffusivities of 5×10^{-6} to 5×10^{-8} cm²/sec for methane and 1×10^{-6} cm²/sec for natural gas, this model gave good agreement for *volume*

diffusion growth of natural gas hydrate films on a water surface. For experimentally obtained diffusivities of 5×10^{-6} to 5×10^{-8} cm²/sec for methane and 1×10^{-6} cm²/sec for natural gas, this model gave good agreement for *volume diffusion* growth of natural gas hydrate films on a water surface.

Maini and Bishnoi (1981) tried to simulate the fate of natural gas bubbles in case of a deep, offshore oil well blow-out by studying formation of hydrates in natural gas bubbles held stationary by downward water flow in a specially designed vertical tunnel. It was observed that hydrates form at the bubble interface at high pressures. However, the rate of conversion was not measured.

Recently, Vysniuskas and Bishnoi (1983, 1985) have studied the kinetics of methane and ethane formation after the start of nucleation in a semibatch stirred tank reactor under isothermal and isobaric conditions. To enable the agitation of the reaction interface by vigorous stirring of water, water was contacted with the gas at temperatures above the freezing point. It was found that though the induction delay time for formation of nuclei depended initially on the history of water sample, it did not affect the overall hydrate formation kinetics, once the nucleation commenced. After an initial induction delay, data was collected only until 5% of the available water was converted, since beyond 5% conversion, the gas-liquid interfacial characteristics were greatly affected by the thickening of water-hydrate slurry. It was found that Arrhenius Law could not be used to describe hydrate growth rate at a function of temperature since it gave a negative value of apparent activation energy, whereas for the activation complex to be unstable, the activation energy should be positive. The growth rate was proportional to the gas-liquid interfacial area and which increased with stirrer speed due to vortex formation.

To describe the gas consumption rate at STP, (r) as a function of gas-liquid interfacial area (a_g), pressure (p), temperature (T) and degree of subcooling (ΔT),

they proposed a semi-empirical model and is given by

$$r = A a_s \exp\left(-\frac{\Delta E_a}{RT}\right) \exp\left(-\frac{a}{\Delta T^b}\right) p^r \quad \dots\dots\dots (4)$$

where

- A = lumped pre-exponential factor.
- ΔE_a = apparent energy of activation
- R = gas constant
- a, b = arbitrary constants
- r = overall order w.r.t. pressure

Table 5 gives the best fit values obtained by Vysniuskas and Bishnoi (1983, 1985) of the rate expression parameters for methane and ethane.

b. Hydrate Formation from Ice Crystals

The first attempt to study hydrate formation from ice crystals was made by Barrer et al (1958, 1962, 1967) when they measured the hydrate formation rate of rare gases A_r , X_e , K_r with ice crystals and ice and chloroform-mixed crystals at low temperatures. They formed fine crystallites by vacuum distilling water and water-chloroform mixtures into the reaction bulb, which was kept immersed in liquid nitrogen. However, the results could not be generalized since surface area was not measured. The hydrate growth was found to increase with temperatures at constant pressure, which might be due to that certain low temperature ice phases exhibit unoccupied hydrate structure.

Fallabella (1975) used an analogous procedure to study the hydrate formation kinetics of natural gases (methane, ethane, ethene, acetylene and carbon dioxide) at low temperatures. Similar to krypton, an induction delay was observed for

TABLE 5: RATE EXPRESSION PARAMETERS FOR METHANE AND ETHANE

	Methane	Ethane
A (cm ³ /cm ² /min/bar)	6.55 x 10 ⁻²⁶	2.4 x10 ⁻²⁹
ΔE_a (kj/gmol)	-106.204 ..	-133.015
r	2.986	2.804
a	0.0778	0.0778
b	2.411	2.411

structure I methane hydrate, whereas, addition of 10% ethane to it, showed no induction delay indicating that ethane has a seeding effect on hydrate nucleation. It was observed that an increase in gas pressure results in a decrease in the induction delay and increase in growth rate. The fractional ice conversion rate was found to be second order w.r.t. unconverted ice and first order w.r.t. the pressure driving force.

$$\therefore - \frac{d(1-x)}{dt} = k(1-x)^2(P - P_{eq.})$$

..... (5)

This expression on integration for the case of isothermal, isobaric conditions gives

$$time t = \left(- \frac{1}{k} \right) \frac{x}{(1-x)} \cdot \frac{1}{P - P_{eq.}}$$

..... (6)

where

- P = gas pressure.
- $P_{eq.}$ = hydrate equilibrium pressure
- k = rate constant
- x = fractional conversion of ice.

Fallabella suggested that hydrate growth was primarily due to high surface mobility of ice at low temperature, since the ice sublimation rate was too slow to account for the growth rate of hydrates. Also, the rate constant vs. temperature relationship indicated a maxima at 183°K and so the Arrhenius type equation was invalid.

In 1970, Miller and Smythe formed hydrates from carbon dioxide gas and finely divided ice (prepared by grinding ice and condensing water from air, both at liquid nitrogen temperature of 78°K) under conditions similar to those existing at Martian ice caps (148°K, 6-5 mb CO₂ partial pressure). Under isothermal conditions,

the reaction was found to be first order w.r.t. pressure, as given by:

$$t = \frac{1}{k} \cdot \ln \left(\frac{P_o - P_\infty}{P - P_\infty} \right) \dots\dots\dots (7)$$

where

- k = rate constant
- P_o = initial CO₂ pressure
- P_∞ = Final (equilibrium) CO₂ pressure
- P = CO₂ pressure at any time t

Using Arrhenius type temperature dependence, the apparent activation energy for CO₂ hydrate formation was found to be 5.9 kcal/gmol which is in reasonable agreement with that observed for the low temperature phase transformation from hexagonal to cubic ice.

Kamath (1984) studied the kinetics of methane hydrate formation from compacted ice crystals formed by condensing water from air at about -20°C and compacting to about 50% porosity inside a vessel. The crystals were initially pressurized to methane pressures of about 7,000 kPa and the temperature raised to just above the melting point of 274°K. The drop in pressure with time was monitored to measure the rate of ice conversion and the experimental results obtained were correlated by two semi-empirical kinetic models. In the first *surface area* model, the rate of hydrate growth was assumed to be proportional to the surface area of ice and the methane concentration driving force.

$$\frac{dx}{dt} = \frac{k S_o V_R M_w n}{M_o} (1 - x)^{\frac{1}{2}} \left(\frac{P_o}{Z_o RT} - \frac{P_e}{Z_e RT} - \frac{M_o x}{V_R M_w n} \right) \dots\dots\dots (8)$$

where

- S_o = initial surface area of ice crystals
- x = fractional ice conversion
- t = time
- k = rate constant
- M_w = molecular weight of water
- T = temperature
- R = gas constant
- M_o = initial mass of ice
- n = hydrate number
- V_R = volume of pressure vessel
- P_o, P_e = initial and equilibrium pressure
- Z_o, Z_e = initial and equilibrium compressibility factor

Numerical integration of the expression using the value of the temperature dependent lumped parameter kS_o between 0.0125 hr⁻¹ and 0.038 hr⁻¹ gave good agreement with the experimental conversion data.

In the volume model, it is assumed that the rate is considered proportional to the amount of unconverted ice rather than the surface area of ice. In this case,

$$\frac{dx}{dt} = k_2 n (1 - x) \left(\frac{P_o}{Z_o R T} - \frac{P_o}{Z_e R T} - \frac{M_o x}{V_R M_w n} \right) \quad \dots \quad (9)$$

The expression was integrated and an analytical solution was obtained. For $k_2 = 2.439$ cc/gmol water/hr, the model give a good agreement with the experimental results with average error of ± 8.8 percent. For methane hydrate formation in unconsolidated sediments, the value of k_2 was found to be a function of the percentage of sand in the unconsolidated core.

The first attempt to quantify the surface area of the ice crystals used for hydrate formation was by Nair and Adamson (1970) who used the BET method to measure the surface area. The ice crystals were formed by condensing superheated steam at liquid nitrogen temperatures. The measurement of adsorption isotherms for nitrogen, argon and carbon dioxide gave surface areas are valid only at low temperatures and they can be significantly decreased by using different methods of forming ice crystals or by annealing at high temperatures.

Wright (1986) developed a new experimental technique to measure the rate of hydrate formation of non-condensable gases like methane from melting ice as a function of pressure and surface. He found that the methane hydrate growth rate was gas diffusion limited and applied this technique to determine the effective diffusivity of methane within the structure I methane hydrate film. It was assumed that molar rate of methane hydrate growth per unit of active ice surface area (r_H) is equal to the molar rate of diffusion of methane molecules from the gas phase, through the hydrate crystal film to nucleation sites on the ice surface and can be expressed i.t.o. the molar ice conversion rate per unit surface area by

$$V_H = - \frac{1}{n_H s} \frac{dni}{dt} = \left(\frac{D}{RT} \right) \left(- \frac{dP}{dz} \right) \quad \dots\dots\dots (10)$$

where D is the effective diffusivity based on a nonporous hydrate film and dP/dz is the methane gas pressure gradient within the hydrate film.

6. STUDIES ON HYDRATE FORMATION, MODELLING AND PHYSICAL CHARACTERIZATION

A. Introduction

In the early years, hydrates were primarily studied to determine operating conditions to prevent their formation in natural gas pipelines. Thus, efforts were concentrated on defining the vapor-water hydrate equilibrium conditions for binary mixtures of pure gas and water, and also for a few tertiary mixtures. In the 50's, Katz (1959), Scauzillo (1956) and later Koledezni (1970) found that the addition of a non-hydrate forming compound like NaCl or ethanol to the water phase, at a given pressure lowers the hydrate forming temperature. Similar "anti-freeze" effect was observed when the non-hydrate forming compound was added to the gas phase. This early work has been reviewed in detail by Katz et al (1959), Byk & Fomina (1968) and API Technical Data Book (1970).

B. Studies on Hydrate Formation

Extensive literature is available regarding techniques of hydrate formation. In most instances, the experiments and apparatus were designed with the aim of determining:

- a) Pressure-temperature equilibrium data as a function of gas composition.
- b) The composition of the hydrate phase.
- c) The rate of hydrate formation.

Also, it is seen that most of the hydrate data was obtained under such conditions of pressure and temperature that the hydrate formers are in the vapor phase. These have been very well reviewed by Katz et al (1959) and others (Byk and Fomina, 1968; Van der Waal and Platteau, 1959; API Technical Data Book, 1970). Kobayashi et al (1949, 1955) obtained three phase VL_1H equilibrium data for pure methane at pressures up to 60,000 psi, whereas Wilcox et al (1941), Reamer et al

(1952), and Teodorovich (1957) studied paraffinic and olefinic hydrates. Table 6 provides hydrate forming conditions for pure gases. Gaseous mixtures of methane and propane have been studied by Campbell and McLeod (1961) and also Carson and Katz (1966) who reported four phase VL_1L_2H equilibrium point data for methane-propane mixtures.

As far as the formation of hydrates from liquid hydrate formers is concerned, the only studies reported are those for pure liquids like propane by (Wilcox et al, 1941) and ethane, propylene, propane (by Reamer et al, 1952), refrigerants freon (Katz et al, 1959, 1975, 1973) and methyl chloride (Chinworth et al, 1967), an exception being study of propane-propylene liquid mixtures (Wilcox et al, 1952). The remaining studies of hydrate formation from liquid mixtures deal either with the determination of quadruple point VL_1L_2H lows or the effect of non-hydrate formers on it, e.g.: $CH_4-C_3H_6$, $CH_3Cl - CHCl_3$ and binary mixtures of C_2H_5Cl with $CHCl_3$, CH_3CHCl_2 , $(CH_2Cl)_2$, CCl_4 , CS_2 , and C_6H_6 . Tables 7, 8, and 9 give a brief summary of studies on binary, ternary, and quaternary systems of hydrates. From these studies it is possible to say in general that,

- a) For pure hydrate forming gases which have critical temperatures below $32^\circ F$, hydrates can be formed under two or three phase conditions, only.
- b) For pure hydrate formers having critical temperatures greater than $32^\circ F$, there exists a four phase VL_1L_2H equilibrium temperature above which hydrates cannot be formed, i.e. the three-phase L_1L_2H equilibrium hydrate curves are nearly vertical on a P-T diagram, e.g. propane.
- c) Similarly, the three-phase L_1L_2H equilibrium hydrates curves on a P-T diagram for a binary liquid mixture of hydrate formers, are nearly vertical if both of them stabilize similar hydrate structures by occupying similar cavities, e.g. propane-propylene mixture (Wilcox et al, 1961).

TABLE 6: HYDRATE FORMING CONDITIONS FOR PURE GASES
(after Kamath (1984))

Gas	a	b	Temp Range (°C)
Methane	16.717	1886.79	-25 to 0
	38.980	8533.80	> 0
Ethane	17.511	3106.56	-25 to 0
	66.273	10626.25	> 0
Propane	17.156	3269.65	-25 to 0
	67.130	16921.86	> 0
Isobutane	18.950	3887.32	-25 to 0
	61.760	15571.63	> 0
Carbon Dioxide	18.596	3161.61	-25 to 0
	66.580	10260.28	0 to 11
Nitrogen	15.129	1506.28	-25 to 0
	37.808	7688.63	0 to 25
Hydrogen Sulphide	16.560	3270.61	-25 to 0
	36.828	8266.10	0 to 25

p = Dissociation Pressure in kPa

T = Temperature, °K

$$T = P = \exp\left(a + \frac{b}{T}\right)$$

TABLE 7: STUDY OF BINARY SYSTEMS OF HYDRATES (WITH WATER)

SYSTEM	REFERENCES
1) Methane	Villard (1888) Deaton and Frost (1940) Kobayashi and Katz (JPT, AIME - 1949) Campbell and McLeod (1961) Marshall et al (1964) Roberts et al (1941) Kamath (1984)
2) Ethane	Villard (1888) Roberts et al (1941) Deaton and Frost (1940-a) Reamer et al (1952)
3) Acetylene	Calletet (19) Villard (1888-9)
4) Ethylene	Van Cleef and Drepen (1962) Villard (1888) Deaton and Frost (1940) Kobayashi and Katz (1949) Diepen and Scheffer (1950) Reamer et al (1952) Snell et al (1961)
5) Propane	Villard (1888) Deaton and Frost (1940-a, 1941) Reamer et al (1952) Teodorowich (1957) Wilcox et al (1941) Holder and Godbole (1982) Kamath (1984)
6) Cyclopropane	Hafemann (1969)
7) Propylene	Reamer et al (1952) Clarke et al (1964) Byk et al (1955)
8) Isobutane	Wu et al (1976) Holder and Godbole (1982)
9) Normal Butane	Schneider and Ferrar (1968) Uchida and Hayano (1967) McKetta and Katz (1968) Ng and Robinson (1976)
10) Cis and Trans-2-Butane	Holder and Kamath (1984)
11) Dichloroethane	Garg (1979)

TABLE 8: TERNARY SYSTEMS OF HYDRATES (WITH WATER)

SYSTEM	REFERENCES
1) Methane-Ethane	Holder and Grigoriou (1980)
2) Methane-Ethylene	Snell et al (1961)
3) Methane-Propane	Verma (1976)
4) Methane-Isobutane	Wu et al (1976)
5) Methane-Butane	McKetta and Katz (1968) John and Holder (1982) Ng and Robinson (1976)
6) Methane-Hydrogen Sulphide	Noaker and Katz (1956)
7) Methane-Carbon Dioxide	Unruh and Katz (1949)
8) Methane-Ci-2-Butene	Holder and Kamath (1984)
9) Methane-Trans-2-Butene	Holder and Kamath (1984)
10)Methane-Nitrogen	Jhaweri and Robinson (1965)
11)Methane-Ar-Kn	Holder et al (1980)
12)Methane-Hydrogen Sulphide	Noaker and Katz (1956)
13)Methane-Propylene	Otto and Robinson (1960)
14)Methane-Sulphur Hexafluoride	Sortland and Robinson (1964)
15)Methane-Carbon Dioxide	Unruh and Katz (1949)
16)Methylene Chloride and Chloroform	Tester and Wiegardt (1969)
17)Propane-Propylene	
18)Propane-Butane	Kamath (1984) Paranjpe et al (1987)
19)Propane-Isobutane	Kamath et al 91982) Patil (1987)
20)Propane-Trans-2-Butane	Kamath et al (1982)
21)Propane-CO ₂	Robinson & Mehta (1971)
22)Propane-Hydrogen Sulphide	Platteeuw and Van DerWaals (1959)
23)N-Butane-Isobutane	Rouher and Marsh (1952)

TABLE 8 Continued.

SYSTEM	REFERENCES
12)Carbon Dioxide	Wiebe, R. (1961) Unruh and Katz (1969) Deaton and Frost (1940-a) Bozzo et al (1973)
13)Chlorine	Davy (1810) Marsh (1952)
14)Sulphur Dioxide	Tamman and Kreige (1955)
15)Hydrogen	de Forcrand & Villard (1888)
16)Nitrogen	Van Cleef and Diepen (1960,65)
17)Oxygen	Van Cleef and Diepen (1960,65)
18)Bromine	Dyadin and Aladko (1977)
19)Xenon	Garg (1977)
20)With Brine and Ethanol Solutions	Kobayashi et al (1957)

TABLE 9: FOUR COMPONENT SYSTEMS OF HYDRATES (WITH WATER)

SYSTEM	REFERENCE
1) Methane-Ethane-Propane	Snell et al (1961)
2) Methane, H ₂ S and CO ₂	Robinson and Hutton (1967)
3) Methane, Propane and I-Butane	Patil (1987)
4) Methane, Propane and N-Butane	Paranjpe et al (1987)

- d) Due to "antifreeze" effect, non-hydrate forming liquids like benzene lower the quadruple point VL_1L_2H temperature.

One of the most widely used techniques for determining the pressure-temperature data is to contact the gas and water in a high pressure glass window cell through which hydrate crystals can be seen. For pressures up to approximately 70 MPa, the equilibrium point at which the hydrates form, can be determined by visual observation (Holder 1976, Kobayashi, 1955). Beyond these pressures, glass windows are not suitable. Similarly, in measurements below the ice point, the presence of ice makes the visual detection of ice like hydrate very difficult. In such cases, the technique commonly employed is to form large quantities of hydrates at low temperatures. (Marshall et al, 1964). The hydrate formation process is usually accompanied by a decrease in pressure, as the gas molecules enter the denser hydrate phase. An increase in temperature now causes the hydrates to decompose, thereby increasing the corresponding pressure. The equilibrium point is considered as that point at which the pressure-temperature curve breaks indicating the end of hydrate dissociation.

A common technique of determining the composition of pure gas-hydrates is to measure the amount of gas needed to convert a known weight of water into solid hydrate. A drawback of this method is that some water, occluded within the hydrate crystal matrix during crystal growth, is not available for hydrate formation, which can be partially overcome, e.g. by breaking the crystals in a ball mill. Ceccotti (1966) formed hydrates on a silver iodide coated tube, directly from gases saturated with water. However, this method also results in occlusion of water, condensed from the vapor phase or forced stabilization of a new hydrate crystal structure. Barrer et al (1962) determined the composition of hydrates from pure gases by monitoring the concentration change of a tracer or water soluble non-hydrate forming salt in water. In this method, it is necessary to account for the effect of

dissolved solids on hydrate equilibrium for greater accuracy. For a gaseous mixture of hydrate formers, the only technique is to melt the hydrate crystals and analyse the gas evolved. However, there might be errors due to water occlusion in hydrate crystal matrix.

For large gas molecules that can only fit in large cavities, the fractional occupancy θ of the gas molecules in the hydrate can be directly obtained from the hydrate composition. This enables the calculations of chemical potential difference for hydrates $\Delta\mu_H$ from the van der Waal and Platteauw model, without calculating the Langmuir coefficients.

For temperatures below the ice points, Holder and Godbole (1982) measured VIH dissociation pressures for propane and iso-butane hydrates at temperatures as low as -22°C using a gravimetric technique. The hydrate formation was detected by employing a sensitive electrobalance capable of measuring weights up to 10^{-4} gms.

Kaplan (1976), Evrenos (1971) and Stoll et al (1971), while studying thermal and acoustic properties of gas hydrate sediments, formed hydrates by passing the gas through a column of granular aggregates of water-saturated sand. Subsequently, Stoll and Bryan (1979) employed a pressure vessel with provision for stirring and compacting to form large cores of pure propane hydrates.

Kamath (1984) studied formation and measurement of hydrate dissociation in the core holder, by forming hydrate cores and dissociating these cores by hot water injection method.

C. Modelling of Dissociation of In-Situ Hydrate

One of the first attempts to view hydrate dissociation as a moving-boundary process was by Cherski and Pondarev (1972), who, however, failed to provide a complete solution. Kamath et al (1984) conducted interfacial heat transfer studies during dissociation of propane hydrates and developed an experimental technique

to measure the rate of heat transfer during dissociation of the solid hydrate phase simultaneously into gas and liquid phases. They showed that the heat transfer rate was a power function of ΔT , the temperature difference between the (warm) bulk heating fluid and the (cold) hydrate surface undergoing phase change. The heat transfer correlation developed was found analogous to that for heat transfer during nucleate boiling of liquids. Later, Kamath and Holder (1987) studied the dissociation heat transfer characteristics of methane hydrates and found that the nucleate boiling analogy could be extended to methane hydrates too. A unified heat transfer correlation for both methane and propane hydrates was developed and, at a fixed ΔT , the heat flux density for propane hydrates was found to be 2 to 2.5 times higher than that for methane hydrates.

Selim and Sloan (1985) modelled the dissociation of a pure hydrate, by assuming that a heat flux is incident on a semi-infinite planar medium with constant physical properties. They considered the hydrate dissociation as a moving boundary ablation process, where it is assumed that the water formed due to dissociation is immediately blown away from the surface by the produced gas.

Ullrich et al (1987) obtained experimental data on rate of dissociation of methane hydrates. The dissociation experiments were conducted using a resistance heater of known heat flux, and the hydrate mass loss measurements were made with an electrobalance. The dissociation process was described by a mathematical model and the agreement between the model and the data was found to be within 10%.

Recently, Selim and Sloan (1987) have modelled hydrate dissociation by thermal stimulation in porous media, wherein the dissociation of hydrate to gas and water is assumed to take place at a moving dissociation boundary. A similarity solution to the conservation equation was obtained and parametric studies were made, which indicated that the hydrate dissociation rate in sediments is strongly

influenced by the thermal properties of the system and the porosity of porous medium. For thermal stimulation of hydrates, the average value of the energy efficiency ratio indicated that the heating value of the produced gas was nine times the heat input during dissociation.

D. Physical Characterization of Hydrates

The physical characterization of hydrates is quite important for development of exploration and production techniques. Numerous studies have been done in the past to study various physico-chemical properties of hydrates such as thermal conductivity, dielectric relaxation, acoustic velocity, electrical property measurements, etc. A summary of studies of physico-chemical properties of gas hydrates is presented in Table 10.

Water Content of Gases in Equilibrium with Hydrates

One of the important specifications in the gas processing industry, for the elimination of hydrates from natural gas operations is the water content of gases or fluids, in equilibrium with hydrates. Though the equilibration process to eliminate the metastable liquid water system is difficult and the experiments are time consuming, it has been successfully accomplished. (Aayogi et al, 1979 and Sloan, 1982). In the past, the measurements of water content of gas in equilibrium only with hydrates in two phase region gave less accurate results due to the fact that metastable liquid water could well extend into the gas-hydrate region and also, large amount of gas in equilibrium with hydrates, was required.

One of the first attempts to measure water content of gases was by Laulhere and Briscoe (1939) who employed an adsorption train gravimetric method for determination of water content of natural gas at hydrate conditions. Later, Deaton and Frost (1946), Records and Seely (1951) employed the Bureau of Mines ASTM

**TABLE 10: STUDIES ON PHYSICAL & CHEMICAL PROPERTIES OF
GAS HYDRATES**

PROPERTY	REFERENCE
a) Thermal Conductivity	Cook (1981) Dharmawardana (1983) Russ (1981,1982)
b) Dielectric Relaxation	Gough (1977, 1978) Hawkins and Davidson (1966)
c) Dew Point of Natural Gases in Hydrate Region	Kobayashi and Katz (1955)
d) Acoustic Velocity & Electrical Properties	Lawson (1984) Kieffe () Whiffen (1982)
e) Relative Permeability to Gas	Leas (1986)
f) Sonic and Resistivity Measurements	Pearson (1983)
g) Heat Capacity	Ross (1982)
h) Surface Tension	Sada (1984)
i) Anamalous Wave Velocities	Stoll (1971)
j) Speed of Longitudinal Sound	Whalley (1980)
k) Physical Properties of Sediments	Stoll (1971)

dewpoint tester combined with the vapor pressure of liquid water. Deaton and Frost (1946), McCarthy et al (1950), McKetta and Wehe (1958), and Laughlin (1969) presented water content charts for natural gas in both gas-liquid region and the gas hydrate region. The water content of gas in equilibrium with hydrates was thought to be considerably lower than the water content of natural gas in equilibrium with metastable liquid water.

- Sloan et al (1976) successfully eliminated the errors arising due to the unusual metastability of liquid water in the gas-hydrate and developed a chromatographic technique for determining the water content of gas in equilibrium with its hydrate, above 32°F up to 1500 psig. For methane, it was found that in order to prevent hydrate formation the water content of methane should be significantly less than that determined from the water content charts. Sloan et al (1978) also obtained an improved value of the vapor pressure (chemical potential) of the metastable empty hydrate, which has been often used in hydrate thermodynamic calculations (Sloan et al, 1976; Aoyagi et al, 1979; Song and Kobayashi, 1981; Holder, 1981; Sloan, 1982).

- Aoyagi et al (1980), while studying water content of methane gas in equilibrium with hydrate, found deviations, from the existing water content charts, of the water content of methane gas at initial hydrate formation condition and which increased with decrease in temperature. Also, the measurements of water content of a simulated lean CO₂ Prudhoe Bay gas and simulated CO₂-rich Prudhoe Bay gas indicated that the water content isobars of the latter converge at lower temperatures, and cross at still lower temperatures.

7. Experimental Techniques of Hydrate Formation

In this section, the various experimental techniques employed for hydrate formation studies have been discussed in detail.

Holder and Godbole (1982) used a gravimetric technique to study VIH data for pure isobutane. As shown in Figure 4, it consists of an electronic balance enclosed in a vacuum head with two inlets to which 42mm diameter hangdown tubes are fitted. The sample can be attached to a suspension wire which is enclosed in the tube and pure gases at any desired pressure (less than 100 kpa) can be admitted through ports. A fine copper wire mesh saturated with distilled water was attached to one suspension wire, whereas an aluminium pan was attached to the other wire to counterbalance the weight of the copper wire mesh and water. The sample weights were displayed on a panel display meter, on a 100 mg scale. The tube enclosing the suspension wire was immersed in an insulated refrigeration bath of volume 10 liters and which could be controlled to $\pm 0.05^\circ\text{K}$ using a Neslab temperature controller. The actual water sample was about 25 cm below the refrigeration fluid (ethanol) level. Ethanol was extracted from one corner of the bath, pumped through coils in a metal enclosure containing vacuum head and back into the diagonally opposite corner of the bath. Temperature gradients within the system were minimized by cooling the vacuum head, which contained most of the gas. Two platinum resistance thermometers were used for measuring the temperatures, one of which was suspended in the bath, with the sensing element about 10mm from the sample, and the other was inserted into a thermocouple well in the sample tube with its sensing element about 2mm from sample. For pressures above 30 kPa, the temperature readings in the thermowell had to be corrected by 0.1 to 0.3°K. A mercury manometer was used in conjunction with the barometer to measure pressures, which were accurate to 0.2 kPa.

NO.	TITLE
①	GAS CYLINDERS
②	CYLINDER REGULATORS
③	CONTROL VALVE
④	MIXING (SAMPLE) TANK
⑤	PRESSURE REGULATOR
⑥	SHUT IN VALVE
⑦	METAL TO GLASS JOINT
⑧	GLASS REMOVABLE JOINT
⑨	BALANCE
⑩	ETHANOL BATH
⑪	REFRIGERATION UNIT

NO.	TITLE
⑫	PLATINUM RESISTANCE THERMOMETER (100 Ω)
⑬	DIGITAL DISPLAY (0.1°K)
⑭	INSULATION
⑮	MERCURY MANOMETER
⑯	VACUUM PUMP

FIGURE 4: GRAVIMETRIC APPARATUS FOR DETERMINING HYDRATE DISSOCIATION PRESSURE BELOW THE ICE POINT

After suspending a water sample from the balance, the temperature was set to a value below the ice point and the sample was frozen. After evacuating the system to 0.1 kPa, it was filled with water saturated isobutane to the desired pressure. The evacuation/filling procedure was repeated and the temperature lowered to 200°K overnight. A gain in weight of sample of 3 to 10 mg was observed due to hydrate formation. The temperature was increased to about 5°K colder than the estimated dissociation temperature of isobutane and subsequently increased in small temperature increments (0.3°K) until there was a weight loss of 1 to 2 mg, which corresponded to the dissociation temperature of hydrates.

The method can detect the presence of hydrates even in very little quantities, and problems with phase occlusion are avoided, due to the small quantities involved. The method was used to determine the dissociation pressures of isobutane hydrate and of propane hydrate which are useful in calculating gas-water Kihara parameters for these gases.

Kamath (1982) used a modified experimental set up for the studying three phase (VIH) hydrate equilibrium for hydrates of cis and trans-isomers of 2-butene below the ice point (Figure 5). The main hydrate cell was a 300 cc SS sampling cylinder, tightly closed at the bottom end and completely immersed in an insulated ethanol bath. A 0.3175 cm resistance thermometer was inserted into the sampling cylinder and was connected to the top end of the cell through a 0.635 cm tube. The bath was equipped with all necessary auxiliaries such as a refrigeration unit for cooling, an immersion heater for heating the bath, a temperature controller for controlling bath temperature, a circulating pump for ethanol circulation (to reduce temperature gradients) and 2 platinum resistance thermometer which was inserted in the bath connected to a digital temperature display unit. One resistance thermometer was placed in the hydrate cell about 5 cm above bottom and the other was immersed in the bath near the hydrate-forming cell.

**FIGURE 5: EXPERIMENTAL SETUP FOR STUDY OF THREE PHASE
HYDRATE EQUILIBRIUM**

The inlet section of the system had three gas cylinders of propane, cis 2-butene and trans-2-butene respectively with standard pressure regulators and a mixing tank for collecting gas from each cylinder. From the mixing tank, the gas could be passed to the sampling cylinder through the annular tubing inlet section. The outlet section was provided with a mercury manometer, a vacuum pump to evacuate the system, provisions for taking gas samples for analysis and a helium cylinder for pressuring the isolated sample before chromatographic analysis and also as a carrier gas in gas chromatograph.

Initially, a 0.3175 cm tube was introduced into the sampling cylinder, extending up to the top quarter of hydrate cell, and its other end was connected to a conical flask containing distilled water. With the hydrate cell bath temperature maintained at 263°K, the system was pressure tested and a vacuum was applied to boil the water in the conical flask and distill it into the experimental cell. This resulted in the formation of about 50cc of finely divided ice crystals in the hydrate cell. The 0.3175cm tube was then replaced by a 0.3175 cm Platinum resistance thermometer, a pressure test conducted and the entire system was evacuated for 3 hours.

Kamath et al (1984) developed an experimental technique for measuring rates of heat transfer to a solid hydrate phase decomposing into gas and liquid phases simultaneously under controlled pressures and temperatures. As shown in Figure 6, the apparatus consisted of two pressure vessels A and B, designed for pressures up to 13.8 MPa and provided with a removable top flange and a permanent bottom flange. Vessel B was used to form hydrate cores and was provided with a pressure gauge, a coiled tube jacket around it for cooling and independent cooling manifold at the bottom. A temperature gradient was maintained in the hydrate vessel by keeping coolant in manifold colder than that in coils. Vessel A was used to separate the gas and water overflow from vessel B during hydrate dissociation and was

FIGURE 6: EXPERIMENTAL APPARATUS FOR STUDY OF THREE PHASE HEAT TRANSFER DURING HYDRATE DISSOCIATION

provided with a pressure gauge, a heater to maintain bulk water temperature greater than that of hydrate, a Jerguson gauge as a liquid level indicator and a circulating pump to circulate warm water to vessel B for dissociating hydrates. The gas liberated during dissociation was separated from water in vessel A and passed subsequently through a wet test meter.

To form hydrates, a known quantity of frost was added to vessel B, maintained at very low temperatures, in four portions with successive compaction of each of the portions by the piston (to ensure uniform void fraction of 0.4 - 0.5). With bottom frost maintained at 250°K, vessel B was closed evacuated and saturated with a known quantity of liquid propane. The temperature gradient in the frost zone saturates the frost completely and ensures that it is saturated from bottom upwards. To prevent any premature melting of frost, the frost temperature is maintained lower than 273.15°K. After complete saturation of frost, vessel B temperature was raised to 274°K and maintained for more than 24 hours, to promote nucleation and formation of hydrates. Excess propane was distilled off by reducing pressure of vessel B below that of vapor pressure of propane but higher than dissociation pressure of hydrates.

Recently, Paranjpe et al (1987) have studied effect of salinity on phase behavior of gas hydrates for different binary and ternary mixtures of methane, propane, isobutane and n-butane, using an experimental set up similar to that used by Kamath et al (1982). As shown schematically in Figure 7, the hydrate cell consists of a windowed Jerguson gauge of capacity 50cc and capable of withstanding pressures up to 20 MPa, suspended in a constant temperature, insulated both by a lever connected to an in-line gear motor for agitation. The windowed bath is provided with a refrigeration unit, an immersion heater and temperature controller, thermo couples and temperature readout device. The salt

FIGURE 7: EXPERIMENTAL APPARATUS FOR DETERMINATION OF HYDRATE PHASE EQUILIBRIUM

concentrations were measured using Beckmann thermal conductivity bridge and gas analysis was done using a gas chromatograph.

Experiments on hydrate phase equilibrium for several binary and ternary mixtures of methane, propane, isobutane and n-butane were carried out to study the effect of heavier components like isobutane and n-butane on phase behavior of hydrates and are important for accurate prediction of zone of hydrate stability for in-situ hydrates. Also, the effect of salinity on three phase (VL_1H) and four phase (VL_1L_2H) equilibrium conditions for mixtures of propane and n-butane of two different salt concentrations was studied and the data were used to calculate hydrate numbers by extending the Miller and Strong Method (1946) to gas mixtures.

The experimental set up can also be employed for studying the hydrate formation in presence of crude oil, which is discussed below.

Hydrate Formation in Presence of Crude Oil

Recent studies (Collett, 1985) have indicated that gas hydrates are present in conjunction with heavy oils and tar sands in the southwest up-dip continuation of West Sak and Ugnu formations in the Kuparak river unit, North Slope of Alaska. With the advent of ARCO-Alaska's thermal recovery pilot plant in the West Sak sands (OGI Report, 1983), it is of increasing importance to establish hydrate phase equilibrium conditions for light gases, brine and oils found in such regions.

The experimental procedure for determining the three phase (VL_1H_1VIH) and four phase (VL_1L_2H) hydrate forming conditions of crude oil-natural gas mixture will be the same as that for gas-water mixtures (Patil, 1987). In this case, the bubble point curve for crude oil-natural gas mixture can also be determined along with the pressure-temperature-gas and oil compositions.

The crude oil mixture and the gas mixture has to be added quantitatively from the recombination apparatus, which recombines dead oil with its lighter components, to the main hydrate chamber containing water or brine. The bubble point pressure can then be determined for various temperatures by first fixing the temperature and pressurizing the hydrate cell until only a very small gas bubble remains. After allowing sufficient for equilibration by rocking the hydrate cell, the pressure can be increased in steps at certain time intervals until the bubble clearly disappears at the bubble point pressure. The temperature of the system is then lowered until a large quantity of hydrate dissociates from the mixture of oil and water. The hydrate cell is treated until very few crystals are left. The system slowly cooled to the predetermined temperature and the four phase water-liquid hydrocarbon-vapor-hydrate equilibrium pressure is determined. The above procedure can then be repeated to obtain data under well mixed equilibrium conditions.

Past studies (Katz, 1971) have shown that the presence of hydrates along with oil can denude a crude oil of its natural gas constituents, resulting in a decrease in production due to viscosity increase and pore blockage and due to radial lowering of vapor pressure of oil (Holder, 1976). The above experimental apparatus can also be used to quantify the effect of hydrate formation on crude oil properties and to predict denuding effects due to hydrate formation by employing the following procedure.

Initially, the various properties of the oil to be tested, like viscosity, specific gravity, bubble point pressure, gas composition and crude oil composition are measured. Hydrates can then formed in presence of crude oil by following the same procedure as used by Holder (1976), and the pressure and temperature conditions for hydrate formation can be determined. At the end of the experiment, the oil can be separated from hydrates and the above properties determined. This data can be

employed to quantify the effect of hydrates on crude oil properties and denuding of oil, and can be useful for developing guidelines for thermal recovery studies, e.g. thermal recovery in West Sak and Ugnu reservoirs.

Study of Hydrate Cores in Unconsolidated Sands

The recovery of natural gas hydrates in the Arctic can be accomplished by the use of hydrate dissociating agents like methanol, brine, hot water, steam injection or by depressurization method when hydrates coexist with a gas cap. To develop methods for hydrate recovery, baseline experimental data are essential. Kamath (1984) studied hydrate dissociation in laboratory synthesized hydrate cores by hot water injection method. For modelling hydrate recovery by different methods, a similar study for other dissociation mechanisms is necessary as also the study of hydrate formation and dissociation in consolidated or unconsolidated sand cores. The following procedure can be followed for hydrate core studies and for studying effect of hydrate formation or dissociation on change in permeability of porous rock.

1. Form hydrates in unconsolidated sand cores.
2. Measure permeability of hydrate cores and study effect of hydrate saturation on permeability of cores.
3. Measure hydrate formation rates under varying gas flow rate, pressure, temperature conditions and study kinetics of hydrate formation.
4. Measure hydrate dissociation rates, heat transfer rate and quantify convection effects during dissociation of hydrates like brine, hot water, and steam injection and depressurization, since previous hydrate models have neglected the convection effect and considered heat conduction as the sole mechanism of heat transfer.

The experimental set up (Figure 8) consists of a specially designed hydrate cell equipped with a cooling jacket through which coolant is circulated. The bath circulator can be maintained at a constant temperature with the help of a temperature controller. The core holder has three parts to monitor the pressure drop across the hydrate core for permeability determination. In addition, three temperature ports are provided to obtain temperature profiles in the hydrate zone and dissociated zone during the dissociation run, and the entire core holder well insulated, to minimize heat losses to the surrounding area. The inlet gas in core holder passes through the bottom port by means of three concentric tubes connected to three gas spargers within the core. Such a design provides a flexible mechanism to overcome problems of core plugging due to hydrate formation. The flow rates of inlet gas and outlet gas-water mixture can be measured by online gas flow meters, whereas a mass flow controller can be used to keep the inlet gas flowrate constant. The outlet gas is compressed and recirculated back into the core holder with a gas compressor, and the downstream pressure of the coreholder is kept constant with a back pressure regulator. Other auxiliary units of the setup include: a gas-water separator, wet test gas flow meter to measure gas production during dissociation, injection fluid reservoir with liquid level indicator, a steam generator, etc.

The core is initially packed with 20 mesh size sand of known porosity and is saturated with water after evacuation. The core is then saturated by methane flowing at a constant rate from a cylinder. From the pressure drops and gas flow rates, absolute permeabilities can be computed. The outlet gas is then compressed to a pressure higher than the core holder pressure thus maintaining the flow of gas in the system. The gas flow rate is controlled by means of flow control and monitored by means of a flow meter. Two inline filters are installed at either end of core holder, housing a teflon membrane which prevents water from escaping from

1. Temperature Controller
2. Methanol Bath
3. Refrigeration Coils
4. Heater
5. Digital Temp Indicator
6. Core Holder
- 7,8,9. Pressure Transducers
10. To Methanol Bath
11. Pressure Indicator
12. Gas Flow Meter
13. Gas Cylinder
14. Wet Test Flow Meter
15. Water Tank
16. Gas Water Separator
17. Back Pressure Regulator
18. Pressure Gauge
19. Back Pressure Regulator
20. Moist Trap
21. Temperature Control
22. Gas Flow Meter
23. Gas Flow Control
24. To Vacuum Pump
25. Water Flow Meter
26. Water Pump
27. Pressure Vessel

FIGURE 8: EXPERIMENTAL SETUP FOR STUDY OF HYDRATE CORES IN UNCONSOLIDATED SANDS

the core holder during hydrate formation.

8. THERMODYNAMICS OF GAS HYDRATES

Several methods have been reported in literature for the prediction of hydrate phase equilibria. One of the earliest methods suggested for prediction of dissociation pressures, the pressure at which the nucleation of hydrate crystals begins, was the K value method of Katz (1944). In this method, analogous to vapor-liquid equilibria, the hydrate equilibria is characterized by a vapor-solid equilibrium constant K_{usi} given by,

$$K_{us,i} = \frac{y_i}{x_i} \quad \dots\dots\dots (11)$$

where y_i and x_i are the vapor phase and solid phase mole fractions, respectively, of the i th component on a dry basis. K_{us} is a function of temperature and pressure and can be calculated from experimental hydrate data by using the criteria

$$\sum_i \frac{y_i}{K_{usi}} = 1 \quad \dots\dots\dots (12)$$

However, this method is no longer used as it suffers from the disadvantages that the experimental data has been used to determine and extrapolate K_{usi} values are not accurate and they do not distinguish between the two hydrate structures. Also, K_{usi} is not a function of gas composition. The K value charts have very large errors associated with predictions.

The first attempt of theoretical studies on hydrates was reported in the late 50's and early 60's when Van der Waals and Platteau (1959) presented a basic

statistical model for predicting hydrate equilibrium based on the crystal structure of hydrates. Their model was based on the following assumptions:

- a. Each hydrate cavity can be occupied by either zero or one gas molecule only and this molecule is localized within the cavity.
- b. The cage is much larger in all dimensions than the largest dimension of the gas molecule, i.e., the gas molecule entrapped has the same rotational freedom as it would in the gas phase and does not distort the cavity. This assumption is not valid for larger molecules like propane and isobutane.
- c. The mutual interaction between the solute (gas) molecules is negligible and the only interaction of the solute is with its nearest neighbor (water) molecules. In other words, the partition function for the motion of a gas molecule in its cage is independent of the number of types of gas molecules present. The distribution of the energy levels occupies by the molecules of a species are described by the work partition function.
- d. The free energy contribution of the host (water) molecules is not affected by the mode of occupation of cavity by dissolved gases.
- e. All the assumption of classical statistics are valid. The water-solute interaction is accurately described by a certain potential function, e.g., the Leonard Jones or the spherical core Kihara potential function.

Consider a hydrate crystal containing N_Q molecules of Q and occupying a volume V at temperature T and crystalized while in equilibrium with the solutes $A \dots, J \dots, M$ having absolute activities $\lambda_A, \dots \lambda_M$. Then the chemical potential of a solvent (water) molecule in the hydrate phase is given by

$$\Delta\mu_H = \mu_B - \mu_H = -RT \sum_{j=1}^2 v_j \ln \left(1 - \sum_i \theta_{ij} \right) \dots\dots\dots (13)$$

where μ_H and μ_B are the chemical potential of the occupied and the unoccupied lattice water, respectively, R is the universal gas constant, v_j is the ratio of the number of j cavities to the number of water molecules in the hydrate phase. The variable θ_{ij} is the fraction of the j cavities occupies by an i type gas molecule, and is give by the Langmuir isotherm

$$\theta_{ij} = \frac{C_{ij} f_i}{1 + \sum C_{ij} f_j} \quad \dots\dots\dots (14)$$

where f_i is the gas phase fugacity of the i th gas species and can be determined by the method of Prausnitz and Chuch (1968). C_{ij} is the Langmuir constant whose value depends only on temperature and potential function parameters and is given by

$$C_{ij} = \frac{4\pi}{RT} \int_{\text{cell radius}} \exp. \left[- \frac{w_{ij}(r)}{RT} r^2 dr \right] \quad \dots\dots\dots (15)$$

where r is the radial position of solute in the cavity, $w_{ij}(r)$ is the smoothed cell potential function.

Since chemical potential of water in equilibrium hydrate phase is equal to that in water rich liquid or ice phase (μ_w), we have

$$\Delta\mu_H = \Delta\mu_w = \mu_B - \mu_w \quad \dots\dots\dots (16)$$

Van der Waals modelled the gas-water interaction using the Leonard-Jones 12-6 potential function and found the dissociation pressure predictions were not quite accurate using literature values of LJ 12-6 constants. Later, Mckoy et al (1963) succeeded in predicting more accurately, the dissociation pressures of polyatomic

gases by employing the Kihara potential function, which is given by

$$\begin{aligned} \Gamma(v)_{H_2O-gas} &= 4\varepsilon \left(\frac{\sigma}{r-2a} \right)^{12} - \left(\frac{\sigma}{r-2a} \right)^6 \text{ for } r > 29 \\ &= \infty \text{ for } r \leq 29 \end{aligned} \quad \dots\dots\dots (17)$$

where

- ε = Kihara energy parameter
- r = Intermolecule separation between gas and water molecules.
- a = radius of core of gas molecule.
- σ = Kihara distance parameter.

Figure 9 shows the Kihara potential function σ , ε/K , and a . Tee et al (1968) have developed correlations for estimating the parameters of the Kihara potential function. However, use of these correlations does not predict hydrate forming conditions accurately. Kobayashi and Katz (1955), Barduhn and Lee (1978) and Nagata and Kobayashi (1960), instead of employing second virial coefficient data, used a semi-empirical approach for predicting hydrate dissociation pressures of methane, Ar and N₂ by fitting the potential function parameters to experimental data. In 1972, Parrish and Prausnitz (1972) extended Kobayashi's work by fitting the potential function parameters and developed a generalized method of prediction of fifteen gases and their mixtures. Though their predictions of pure component data were very accurate, the predictions for mixture dissociation pressure were slightly in error.

In the above cases, it is assumed that the water molecules surrounding the gas molecules are evenly distributed over a sphere whose diameter is average of the

FIGURE 9: KIHARA POTENTIAL FUNCTION

actual cage dimensions. Fester et al (1966) calculated the sum of all gas-water interactions individually by employing the Monte Carlo approach, but with little improvement in the accuracy of the results.

Holder (1976) and Holder and Godbole (1982) employed the Parrish and Prausnitz method for predicting the dissociation pressures of methane, ethane and propane mixtures and obtained optimum values of the different parameters involved in the hydrate model. Ng and Robinson (1977) added another adjustable parameters to obtain improved prediction of multi-component dissociation pressures, and also for prediction of conditions of hydrate formation from condensed systems.

Although the basic van der Waal model based on structure of hydrates, contributed significantly to the theory of hydrate compounds the original model has undergone many modifications in the last decade. In the Van der Wall model it is assumed that only the neighboring interactions between gas and water molecules are important. John and Holder (1981, 1982) and John et al (1985) critically examined hydrate phase equilibrium theory of Van der Waal and Plateau and found that the equilibrium calculations were significantly affected by the interactions of the guest molecules with those host molecules of the hydrate lattice, which are not in their immediate vicinity. They also defined second and third shells of water molecules for the four cavities of hydrate structures. For large asymmetric guest molecules whose internal motion is likely to be restricted, they used a modified semi-empirical method for calculating Langmuir constants which gave improved predictions of hydrate equilibrium. However, this method suffers from the disadvantage that each gas species has to be treated according to its shape, i.e., linear, spherical, etc. A study was also made of restrictions to molecular rotations and of molecular locations within hydrate cavities caused by them.

John et al (1985) have suggested that the overall cell potential is represented by assuming three different shell contributions to the overall gas water interactions and is given by

$$w(r) = w_1(r) + w_2(r) + w_3(r) \quad \text{..... (18)}$$

where w_1 , w_2 , w_3 represent first, second and third shell of water molecule, respectively.

To account for the asymmetric gas-water interactions for non-spherical gas molecules like n- and isobutane, Holder and John et al (1985) introduced a novel approach called the Qstar correlation method for determination of true Langmuir constant. Q represents an empirical correction factor for Langmuir constant due to restricted motion of gas molecules and the corresponding state correlation for Q function is given by

$$Q = \exp. \left[-A_o \left\{ w \left(\frac{\sigma}{R-a} \right) \left(\frac{\epsilon}{KT} \right) \right\}^n \right] \quad \text{..... (19)}$$

where A_o and n are empirical parameters and depends on the particular cavity. The true Langmuir constant C is then given by

$$C = C^* Q^* \quad \text{..... (20)}$$

This approach is recommended for hydrate phase equilibrium studies as it provides sufficiently accurate predictions.

Kamath (1982) used the Q star correlation method developed by John and Holder (1982) and extended it to optimize Kihara parameters for n-Butane from their experimental data.

9. DETECTION AND EVALUATION OF IN-SITU NATURAL GAS HYDRATES

A. INTRODUCTION

Natural gas hydrates have been studied in the past primarily to determine how to avoid their formation in natural gas transmission lines (Hammerschmidt, 1935). Also, the in-situ natural gas hydrates represent a potential drilling hazard and as such their detection of vital importance in regions where they occur. In addition, they may in the future provide a valuable resource for natural gas. Significant quantities of gas hydrates have been detected in many permafrost regions of the world, in West Siberia (Makagon, 1970), in the Mckenzie Delta of Canada, and on the North Slope of Alaska, as well as in the warmer offshore regions such as the Gulf of Mexico, Blake Bahama Outer Ridge and Mid-American Trench. The existence of hydrates in these areas has been confirmed from well log responses in the Mckenzie Delta (Bily and Dick, 1974), Prudhoe Bay and Kuparuk field (Osterkamp and Payne, 1981) as well as retrieved from Gulf of Mexico (Brooks et al, 1984). Also, extensive gas hydrates can exist in many areas beneath the sea floor (Makagon, 1970). The occurrence of hydrates in deep sea sediments in essentially tropical regions like the Gulf of Oman and off the northern coast of Columbia and Panama has also been indicated in drilling operations and seismic data. Bily and Dick (1974) provided one of the most conclusive studies on the occurrence and detection of in-situ natural gas hydrates wherein they incorporated well logs, including dual induction, sonic and mud logs as potential hydrate detection devices.

B. MEANS OF DETECTION OF HYDRATE FIELDS

In spite of the fact that the present detection techniques serve to identify the location of hydrate fields, with the increased interest in naturally occurring hydrates, there is a greater need for improved detection and evaluation

methods. The various techniques used to detect the hydrates in the earth are discussed in the following paragraphs.

1. Hydrate Stability Determination

The simplest and quickest way to check the zone of possible gas hydrate occurrence is to examine the zone of gas hydrate stability. For gas hydrates to be stable at a given depth, the earth temperature at that depth should be lower than the equilibrium temperature of hydrates corresponding to the pressure and gas composition conditions. However, the existence of gas hydrate stability conditions is not a necessary and sufficient condition for the existence of hydrates. For hydrates to occur, gas and water should coexist in the zone of hydrate stability.

The stability of gas hydrates in the earth and in the outer regions depends upon several factors such as mean annual surface temperature, geothermal gradients above and below the base of permafrost, salinity, subsurface pressures, gas composition, permafrost depth, pore pressure conditions and soil particle effects. The geothermal gradients and subsurface temperatures in Arctic North Slope regions can be obtained from previous studies (Osterkamp and Payne, 1981) and (Lachenbruch et al, 1985; Lachenbruch et al, 1982; Blanchard and Tailleux, 1982; Ferrigna, 1965; Brewer, 1958; McCarthy, 1952). Also, several thermodynamic studies on the measurement of pressure-temperature relationships for different gas hydrates reported in literature are used for hydrate stability determination (Deaton and Frost, 1946; Kobayashi and Katz, 1955; Wu et al, 1976; Kamath, 1982). Table 11 gives the values of mean annual surface temperature (T_s), permafrost base depth (Z_p), geothermal gradient within permafrost (G_{fr}), and geothermal gradient below the base of the permafrost (G_{th}) in the Prudhoe Bay and Kuparuk - West Sak fields. Godbole et al (1986) have presented a nomogram for the determination of zone of methane hydrate stability (ZMHS) for specific conditions of mean annual surface

**TABLE 11: GEOTHERMAL PROPERTIES FOR PRUDHOE BAY
AND KUPARAK-WEST SAK FIELDS**

PARAMETER	PRUDHOE BAY	WEST SAK AND KUPARAK FIELD
1) Annual Surface Temperature, °C	-10.9	-9.3
2) Permafrost Depth, m	630	682
3) Geothermal Gradient Within Permafrost, °C/100m	1.66	1.75
4) Geothermal Gradient Below Permafrost, °C/100m	2.86	3.03

temperature (T_s), salinity, geothermal gradients (G_{fr} and G_{th}). Osterkamp and Payne (1981) and Zoeller (1984) suggested that subsurface pressure for the shallow unit on the North Slope can be assumed to be in a hydrostatic equilibrium (0.435 psi/ft or 9.84 kPa/m) and have developed a nomogram assuming a hydrostatic variation in pressure. Sensitivity analysis indicates that the zone of hydrostatic stability increases by about 2.75 percent per percent increase in pressure gradient above hydrostatic value.

Evrenos (1971) has shown that the presence of salts in the formation fluids not only depresses the permafrost base temperature but also depresses the equilibrium by hydrate temperature and thus reduces the zone of hydrate stability. An increase in mean annual surface temperature and geothermal gradients lowers the zone of hydrate stability. Similarly, the reduction in ZHS is about 2.3% per 1,000 ppm increase in salinity.

Gas composition strongly influences hydrate stability conditions. The stability of methane hydrate is increasingly affected by the addition of ethane, propane and isobutane. Addition of CO_2 has an effect similar to ethane. A recent study by Kamath et al (1984) of 46 representative wells on the North Slope of Alaska has shown that the presence of small quantities of lighter hydrocarbons like propane, butane, etc. increases the stability of hydrates considerably and needs to be incorporated in the future calculations of hydrate stability.

2. Drilling Response

Severe and gasification, drill stem tests, ore sample studies, etc. can be applied for the detection of hydrates. Cores have been retrieved in Prudhoe Bay (Northwest Eileen State Well #2), Leg 84 of Blake Bahama Outer Ridge (Sloan, 1983) and in the Gulf of Mexico and the offshore region of Guatemala, for core sample studies, etc.

Present techniques like pressure core barrel can be applied for determining the type of hydrate deposit (massive, laminated, modular, etc.).

3. Seismic Profiling

Shiple et al (1979) have presented data which show that many anomalous reflections from the continental slopes and rises have characteristics which can be explained by the formation of gas hydrates. Direct sampling of these horizons is needed to identify them conclusively and to substantiate the physical conditions of formation. It is found that acoustic wave velocities in hydrated sediments are much higher than in hydrate free sediments and can be utilized for detecting the presence of hydrates in suboceanic environment. Tucholke et al (1977) have studied gas hydrate horizons detected in seismic profiler data from the Western North Atlantic, wherein reflecting horizons have anomalously high amplitude. It has been found that these horizons cut across bedding planes in the sediment and are restricted to areas where seismic strata up landward.

4. Wire Line Log Evaluation

Logging of hydrate intervals with conventional logs provides significant information for hydrate identification. High acoustic velocities on sonic logs, high resistivity deflection or dual induction logs, high gas on mud logs, expanded well bore on caliper logs are some of the indications of presence of hydrates. Direct log readings can often lead to misinterpretation of hydrate zones as either free gas zones or permafrost zones, particularly if decomposition has occurred during drilling. Log correlation and analysis provides additional proof of occurrence of hydrate zones. Goodman et al (1982) have presented five log analysis methods for specific application to in-situ hydrates. In this study, a correlation technique based on temperature log has been presented.

Collett and Economides (1983) have reviewed the use of well logs in the detection of hydrates. Collett et al (1983) have presented a technique for confirming the distinction between ice and hydrate, as well as quantification of hydrate deposits, which involves the use of neutron porosity transtime cross plot along with Pickett cross plot. Similar to the neutron porosity correction factor. Collett et al (1984) have outlined a transtime porosity correction factor. They showed that the ratio of compressional velocity in boise core saturated with structure I hydrate to that in boise core saturated with ice at -5°C is 1.18, e.g., an apparent porosity of 0.28 in hydrate saturated zone would be corrected as 0.335. They also evaluated a series of matrix porosities and sonic-velocities for eighteen units in Kuparuk B-1 production well. For a mixture of hydrate-water coexistence, it is possible to calculate the average water saturation, and hence, the average hydrate saturation by use of Pickett cross plots. A similar study of hydrates in Canada is being presently conducted by Judge (1984) and coworkers. In general, the best method for identification and quantification of gas hydrate deposits is to first determine the zone of hydrate stability, and then further determination of hydrates within stability zone by use of well logs.

GEOLOGIC ANALYSIS OF GAS HYDRATE DEPOSITS

Malone et al (1986) have evaluated the geologic factors that control the formation and detection of gas hydrates within offshore (Blake Outer Ridge), as well as onshore (North Slope of Alaska environments). In their study, they concluded that more detailed geology and reservoir data on the known hydrate occurrences, a detailed study of reservoir conditions and laboratory research a detailed analysis of individual targets with high potential for hydrate occurrence and greater drilling to recovery more samples, were necessary for geologic analysis of potential gas hydrate deposits.

10. GAS PRODUCTION FROM HYDRATE RESERVOIRS

The first step in the production of gas from hydrates is the dissociation of hydrates to gas and water. This transformation can be represented as:

$$(\Delta H_n = + 10 - 20 \text{ kcal})$$

where $C_n H_{2n+2}$ represents either methane, ethane or propane and x is called hydrate number and is a measure of the number of moles of water/mole of gas in the hydrate phase. Table 6 gives typical values for x .

The positive value of ΔH indicates that 10-20 kcal of heat must be added to the hydrate reservoir per mole of methane dissociated, a part of which is used in heating up the reservoir to dissociation temperature and the remaining heat is available for achieving the above transformation. In addition, there are heat losses to overburden and underburden formations, and wellbore heat losses. It has been found that heat obtained by burning gas produced from hydrates is nearly ten times that required to dissociate them. Thus, we can conclude that from a thermodynamic point of view, production of gas from hydrates is energy efficient.

The most important factors to be considered for assessing the feasibility of gas production from hydrates are the form in which they exist in the reservoir and the extent of their saturation in the reservoir rock pores (Holder et al, 1984). Hydrates can exist either in association with gas, water, ice, or as 100% hydrates. Other factors which should be considered are reservoir rock properties of hydrated and

hydrate free zones, and heat losses, if any, to overburden and underburden formations.

The quantity of gas that can be produced from a hydrate reservoir will also depend upon how the dissociation of hydrates affects the porosity, permeability, formation structure, etc. of the reservoir. The hydrated gas may be present in the reservoir in consolidated or unconsolidated media. The reservoir character may change drastically with dissociation of hydrates into gas and water (ice). Hence, in order to apply the conventional production techniques to a hydrate reservoir, it is necessary to compare the technical and economic aspects of the various production methods.

Various techniques have been put forward for the production of gas from gas hydrates. These include thermal recovery by injection of steam, hot water, hot brine or fire flooding, depressurization and injection of hydrate inhibitors like methanol or glycol (Halleck et al, 1982; McGuire, 1981; Holder et al, May 1982; Holder et al, Nov. 1982; Bayles et al, 1984; Kamath et al, 1985). These are discussed in the following paragraphs.

a. **Thermal Recovery**

In this method, the dissociation of hydrates to gas and water is accomplished by providing thermal energy in the form of steam, hot water, hot brine or by fire flooding. From a thermodynamic point of view, thermal recovery technique has been found to be viable (Holder et al, 1982), but it may pose problems in the severe conditions where hydrates occur.

Gas production by thermal recovery is illustrated here by considering steam injection. A schematic diagram of thermal recovery by steam injection is shown in Figure 10. Steam is injected into the hydrate reservoir at a specific rate and at a specific temperature in a cyclic manner. Each cycle is considered to be made up of steam injection stage, hydrate dissociation stage and gas production stage

FIGURE 10: SCHEMATIC DIAGRAM OF A WELL IN THE ARCTIC REGION

Bayles et al (1984) have developed a model to determine the limits of expected gas production for such single well cyclic steam process. Their results indicate that deeper reservoirs and reservoirs with higher hydrate filled porosity and higher zone thickness result in better gas production, and higher energy efficiency ratios.

McGuire (1981) has developed two models for the production of methane hydrate by hot water injection. The frontal sweep model envisages a production scheme which is similar to steam flooding of a heavy oil reservoir and predicts highly optimistic gas production rates. The fracture flow model simulates gas production from low permeability hydrate reservoirs and predicts the lower limit of hydrate gas production.

Recently, Kamath and Godbole (1985) have suggested the use of hot brine for gas production from hydrate reservoirs. The use of hot brine instead of steam results in lower heat losses, reduced reservoir heating and lower hydrate dissociation energy. For economic viability, they recommended that the hydrate reservoir should possess a porosity of, at least, 15%, minimum hydrate zone thickness of 25 feet, high brine salinity, brine temperature between 250°F and 600°F, and minimum brine injection rates of 5,000 BPD.

Kamath et al (1985) have studied the effect of hydrate dissociation during thermal recovery of heavy oils by steam drive on the North Slope of Alaska. It was found that the presence of hydrates is beneficial for heavy oil recovery and results in improved reservoir heat efficiency, cumulative oil production and higher oil to steam ratio. Also, the generation of gas due to hydrate dissociation results in a higher reservoir pressure, reduced oil viscosity, reduced gravity override and provides gas drive mechanism. However, there is a decrease in steam zone efficiency due to significant loss of steam in dissociated zone.

b. Depressurization

Another method for dissociating hydrates to gas and water is by reduction of pressure. In order that heat flows to the hydrates, a temperature gradient has to be generated between the hydrates and the surrounding media. This is accomplished by reduction of pressure which causes dissociation of hydrates to gas and hence a lowering of temperature of remaining hydrates. The generation of gas in turn, raises the pressure to the vapor pressure of hydrates at the new lower temperature, thus establishing a temperature gradient.

Holder et al (1982) have simulated gas production from a reservoir containing stratified layers of gas hydrates and free gas. The hydrate zone was assumed to be impermeable and hence acted as a gas cap. They showed that the contribution of gas from dissociation of hydrates to the total gas production, increases with production time, and can even reach up to 40% of total production.

McGuire (1981) has presented a depressurization production scheme wherein a fracture is deliberately generated to increase the permeability of the hydrate zone. As per the model, the rate of gas production is a strong function of permeability in the ice zone but is independent of permeability in the hydrate zone. McGuire (1981) has also suggested a *salt-free* technique for melting the ice or hydrate surrounding the fracture and for maintaining the salt concentration in the area sufficient to prevent refreezing for the life of the well. This may enable the production of hydrate gas feasible even temperatures well below 0°C which might not be possible by conventional fracturing techniques.

So far, gas production from a hydrate reservoir only has been considered. Recently, Burshears et al (1986) presented a 2 phase, 3-dimensional, variable composition numerical model for gas production from a conventional gas reservoir in contact with hydrates. They concluded that it is possible to dissociate hydrates without any external energy source. The production of gas from the gas reservoir causes pressure reduction which, in turn, results in dissociation of hydrates to gas

and water by depressurization and consequently a further increase in gas production. Thus, an expected low rate of pressure decrease during production of conventional oil and gas might indicate the existence of hydrates. However, for depressurization the initial temperature of the reservoir should be near or above 32°F. Otherwise, the hydrate would dissociate to gas and ice, which being impermeable prevents further dissociation of hydrates.

C. Unconventional Techniques of Gas Production From Hydrates

A number of unconventional techniques for producing gas from hydrates have been suggested which include solvent injection, salt frac and in-situ combustion. The injection of solvents like methanol or glycols into a hydrate reservoir causes the hydrate to dissociate. An advantage of this technique is that the solvent can be recovered in a production well and recycled.

Another method suggested (McGuire et al, 1981) is the salt frac technique which improves the effectiveness of steam or solvent injection by using salt as a proppant. In the presence of salts, the hydrate stability curve shifts to the left, thus reducing the hydrate dissociation temperature in the thermal injection or reducing the quantity of solvent necessary for hydrate dissociation in the solvent injection technique.

In case of the in-situ combustion method, methane and oxygen are injected into the reservoir and ignited. As a result of controlled combustion of methane within the reservoir, the hydrates dissociate to produce gas.

Some of the unconventional extraction techniques suggested are dissociation of hydrates by microwaves and electrical waves, water jet drilling, burial of radioactive wastes for providing thermal energy for dissociation, reservoir depressurization and sea floor mining (METC Topical Report, 1984).

Some other production techniques suggested by Russian scientists (Krason, 1985) are given below:

- a. By utilizing heat of the formation, e.g., reduction of formation pressure in hydrate deposits by removing fluids.
- b. Reduction of the equilibrium temperature of hydrate dissociation
 - i. by addition of substances that dissolve gas released due to hydrate dissociation, thereby decreasing the partial pressure of gas above hydrates;
 - ii. by injection of non-hydrate forming gases like air.
- c. Simultaneous injection of hot water, believed to exist beneath the hydrate zone and at temperatures above 50°C for dissociation of hydrate.

For marine gas hydrate deposits;

- a. Suction dredging of sediments saturated with hydrate has been suggested. The slurry containing gas, hydrates and sediments are transported to the surface where gas is then separated. However, for producing gas from marine gas hydrate deposits, it is necessary to remove the upper layers of sediments devoid of hydrates, excavate the sediment poorly saturated with hydrate and develop the producing deposits at tens to hundreds of meters from the sea bottom.

Geological Implications

In addition to the temperature and pressure conditions in the hydrate reservoir, geological parameters play an important role in determining the amount of hydrates formed. This, in turn, affects the producibility of gas from a reservoir. One of the most important factors which affects the heat necessary for hydrate dissociation and the flow rate of dissociated gas is reservoir porosity. The efficiency of thermal injection and the thermal properties of the hydrates are determined by

the thermal properties of the hydrate reservoir like heat capacity and enthalpy of reservoir media, etc.

Holder et al (1980) have studied the effect of geological parameters on gas production from in-situ gas hydrates by steam injection recovery technique. Their study indicates that the geological and thermal conditions of the hydrate reservoir play an important role in maximizing thermal recovery of gas by hydrate dissociation.

11. DRILLING IN THE PRESENCE OF HYDRATES

The occurrence of hydrates in wells drilled in the polar region has been well documented. In the past, drilling through hydrate zones has resulted in problems of mud control due to severe mud gasification (Bily and Dick, 1974; Franklin, 1979), and the decomposition of hydrates during drilling has resulted in several gas kicks in the Mckenzie Delta and fires on seismic rigs (Judge, 1984). In addition, fizzed drill cuttings, wellbore freeze up, casing collapse and near blowout situations (Makagon, 1965; Franklin, 1979) have been reported. The low permeability of hydrate reservoirs prevents mud loss and results in the formation of a protective clay coating on well walls. Therefore, drilling through hydrate reservoirs results in decomposition of hydrate and also heats up near-hole hydrate containing rocks. The intergranular bonds weaken, the rock collapses, forming an intensive cavity and may lead to violent degassing, tool sticking and mud blowout (Makagon, 1983).

While drilling through a zone of naturally occurring hydrates, they are exposed to an increased temperature and thereby dissociate into gas and water, providing gas influx in the wellbore. In addition, the introduction of gas for cleaning hole cuttings or for lubrication of the drill bit, reduces hydrostatic pressure of the mud column which further accelerates hydrate dissociation in the vicinity of the wellbore. Rapid dissociation of the hydrate zone can introduce a large gas influx from the dissociated hydrate zone into the wellbore causing a gas kick.

In view of the expected increase in oil and gas exploration in the coming years, particularly in areas of potential hydrate occurrences, it has become increasingly important to use safe drilling practices. One of the standard drilling methods used in the past to overcome severe gasification problems has been to cool the drilling mud and increase the mud density. Though this approach eliminates heat input from the mud to the hydrate zone, it does not succeed in reducing the hydrate zone

temperature primarily due to heat flow from deeper formations and also due to the heat exchange between down flowing drill pipe fluid and returning annulus fluid.

Another approach is to use cooler muds while increasing mud weights. In this case, the dissociation of hydrates during drilling can raise the shut-in pressures under closed in BOP stacks to levels sufficient to fracture formation below the casing shoe. Also, as a result of gas evolution, there is a reduction in mud density, which facilitates entry of free gas from other exposed holes into the drill hole. Goodman (1978) has analyzed the decomposition of hydrates during drilling considering thermal effects only as governed by the pressure-temperature equilibrium curves of hydrates. Factors affecting decomposition of hydrates include mud inlet temperature, flow rate, drilling schedule, geothermal gradient, well configuration, soil properties, etc.

In contrast to the foregoing methods which aim at inhibiting dissociation of in-situ hydrates, Franklin (1980) suggested promotion of the dissociation while the drill pipe is in hole by using lower weight muds. The gasified mud on returning to wellhead is subjected to degassing, cooling and recirculated. Furthermore, the penetration rate is reduced to maintain the gas volume in proportion to the capacity of the available equipment. For replacement of drill bit or for logging purposes, hydrate dissociation can be interrupted by employing heavier muds. This approach has been effectively used for drilling through hydrates in the Canadian Arctic.

Coring hydrates with conventional core equipment can be dangerous with a pressure core barrel. It is necessary to use cool drilling mud. Otherwise, special equipment would be needed at the surface to control the temperature of the hydrate filled core barrel during depressurization (Bily and Dick, 1974). For drilling to deeper depths, hydrate zones should be preferably cased off.

Goodman et al (1979) have simulated the drilling process of a Panarctic well in the arctic offshore which can be used for controlling hydrate dissociation during tripping and setting of the casing. To control the hydrate gas influx, increase the dissociation temperature should be increased by using higher mud weights. This causes a change in hydrate equilibrium conditions, so that further decomposition is prevented. Goodman (1978) has provided guidelines for the type of muds to be used in arctic conditions. Thompson (1985) presented a model for determination of downhole mud temperatures to be used while drilling through non-hydrate zones.

Roadifer et al (1987) have presented an unsteady state, two dimensional (r-z) cylindrical coordinate finite difference simulator for modeling the dissociation of hydrates during drilling, for establishing guidelines for controlling the hydrate dissociation rate and the gas influx at wellbore, and for handling gas realized at the surface. The model determines dissociation rates, gas influx rates for given mud weight, mud temperature and specific reservoir conditions. Furthermore, it enables the determination of optimum mud weight and mud temperature for a given capacity of a degassing unit. Three methods have been suggested to control hydrate dissociation during drilling. These include: reducing mud temperature, increasing circulation rate and increasing mud weight. The specific method or combination to be used depends upon several factors like feasibility, economics and reservoir parameters.

Based on the wellbore heat transfer models of Keller et al (1973), Marshall and Bentsen (1982) and the wellbore hydraulics for newtonian fluids. Bingham plastics and power law fluids (Bourgoyne et al, 1986), Roadifer et al (1987) coupled the wellbore heat transfer and hydraulics with their hydrate dissociation model to model the hydrate dissociation under a wider range of drilling conditions. The model can be used to predict the effects of a wide range of drilling parameters on wellbore temperature, pressure, and subsequently the hydrate dissociation rate for

arctic terrestrial, arctic subsea and subtropic subsea locations. They concluded that for preventing hydrate dissociation:

- a. Turbulent flow conditions should be maintained in the annulus.
- b. Run the casing after potential hydrate zones have been penetrated, if permafrost problems can be avoided.
- c. There should be no casing run to the platform in subsea locations if it is feasible.

For promotion of hydrate dissociation:

- a. Flow through the annulus should be laminar.
- b. The casing should be run to the maximum depth above potential hydrate zones, where feasible.

A series of plots and nomographs have been presented for the determination of potential hydrate zones, selection of drilling parameters, or design of surface equipment for safe drilling through potential hydrate zones. Figure 11 (Godbole et al, 1987), Figure 12 and Figure 13 can be used to determine depths to which hydrates may be expected in arctic subsea and subtropic subsea locations. Figure 14 gives a nomogram for estimating parameters for drilling through hydrates. These can be used for predicting temperature and pressure necessary to keep hydrate dissociation within safe limits of drilling equipment, or vice versa, for design of surface degassing equipment for maximum temperatures and minimum pressures expected to occur over the hydrate zone.

FIGURE 11: NOMOGRAM TO DETERMINE HYDRATE STABILITY
IN ARCTIC ONSHORE REGIONS

FIGURE 12: ZONE OF HYDRATE STABILITY IN THE ARCTIC SUBSEA REGION

FIGURE 13: ZONE OF HYDRATE STABILITY IN THE SUBTROPIC SUBSEA REGION

FIGURE 14: NOMOGRAM FOR ESTIMATION OF PARAMETERS WHILE DRILLING THROUGH HYDRATES

12. POTENTIAL OF HYDRATES AS AN ENERGY RESOURCE

The presence of in-situ natural gas hydrates in Arctic and suboceanic regions has been well documented. Potentially huge deposits of hydrates have been identified in cold regions such as Arctic Alaska, the preliminary estimates for Alaskan onshore and offshore regions being approximately 500 million cubic feet of gas-in-place. (Holder et al, 1984). Hydrates possess several characteristics which make them an attractive alternate source of energy for the future. First of all, hydrates represent a concentrated form of natural gas i.e. one cub feet of hydrate can contain as high as 160-180 ft³ of natural gas. Secondly, they possess an energy content comparable to that of heavy oil. Thus, the energy content of a hydrate reservoir is approximately 45,000 to 60,000 Btu/cubic feet of hydrate. Also, from a thermodynamic viewpoint, the recovery of gas from a hydrate reservoir is an energy efficient process. Thus, only 10% of the energy recoverable from the gas is consumed in recovering it from hydrates.

It is well established that hydrates contain about 10 to 15 weight % natural gas, depending upon the gas composition, and hence they can be considered as a potential energy source in the future if they can be economically recovered. In addition, even the most conservative estimates of natural gas in hydrate form are significantly greater than the conventional gas deposits. Though several recovery schemes like thermal recovery, depressurisation, inhibitor injection etc. have been suggested to recover gas from the hydrates, they have not been found to be economically attractive primarily due to the abundant supplies of conventional gas. With the depletion of the conventional gas resources, there will be an increasing need to develop production technologies to harness this resource, particularly because of its widespread occurrence.

For hydrate production to be feasible, it appears that free gas should be laterally associated with hydrated gas and that too extensively (Franklin, 1980). For

recovering natural gas, Panarctic suggested a novel approach, wherein the dissociation of hydrates is influenced by the free gas laterally associated with it. By employing low weight muds and proper degassing equipment on the surface, they tried to promote early dissociation, while the drill pipe was in the hole. Recently, Roadifer et al (1987) have studied the effect of varying drilling parameters for safe drilling through potential hydrate zones and have provided guidelines for promoting and preventing dissociation.

The heat required to convert the hydrates to gas and water is about 60-120 kJ/mole of gas, which is nearly 10 percent of the heating value of the gas. However, the hydrate dissociation process maybe accompanied by large heat losses to overburden and under formations, which can make the gas production uneconomical. Holder et al (1986) have compared the economics of gas production from hydrate deposits by thermal recovery and depressurisation techniques, on the North Slope of Alaska. Their analysis indicates that thermal techniques are uneconomical even with multiple zones, though depressurisation technique might be feasible. For producing gas from offshore hydrate deposits by the depressurisation technique, the break-even-prices are lower.

For developing viable gas recovery techniques from hydrates, it is necessary to study, in detail, the in-situ nature of hydrates, characteristics of the media in which they occur (like porosity, permeability of hydrated and unhydrated zones), extent of hydrate saturation in the pores of the reservoir, heat requirements for hydrate dissociation and problems associated with production due to low permeabilities and cold environment.

13. PREVENTION OF HYDRATE FORMATION

Though gas hydrates were discovered way back in 1810, the study of gas hydrates did not have any indirect industrial bearing until in 1936. Mammerschmidt (1934) discovered that the plugging of natural gas pipelines was primarily due to the formation of gas hydrates. It was then that the research of hydrates received an impetus and efforts were made to develop techniques to prevent formation of hydrates in natural gas pipelines.

One of the first attempts to study hydrate inhibition technique was in the late 50's, when Scauzillo (1956) investigated the effectiveness of both liquid hydrocarbons and glycols in inhibiting the formation of gas hydrates. He conducted hydrate inhibition tests on three mixtures of natural gas and a saturated hydrocarbon oil in presence of excess brine, and also, on two mixtures of the residue gas and an absorber oil in presence of excess distilled water. He concluded that the hydrate formation temperature of gas was lowered if liquid hydrocarbons are also present in natural gas, and that hydrate formation can be inhibited by glycol solutions. It was also found that the combined effect of liquid hydrocarbons and the aqueous glycol solutions approach additive properties with decrease in gas/oil ratio.

In the late 1970's, Mobil reported the installation of a new methanol injection system to prevent production loss due to hydrate formation in the long flow lines between wells and production platforms in the Gulf of Mexico (Bleakley, 1970). A detailed analysis of the various techniques indicated that the most economically viable technique for prevention of hydrate formation was that of methanol injection directly at the well site. The system was so designed as to inject the optimum amount of methanol at each well head. The injection system was required to be operated only during the colder months of the year since no hydrate formation was found to occur below the Gulf water temperatures of 68°F. Also, no

attempt was made to recover the injected methanol, as it was found to be economically unattractive.

Recently, Menten et al (1981) have proposed a theoretical method to predict the effect of inhibitors on the conditions of formation of natural gas hydrates. The method can be used to predict the effect of inhibitors (like KCl , $CaCl_2$, CH_3OH and C_2H_5OH) using existing hydrate parameters and literature data and can be readily extended to other inhibitors and gas mixtures.

To prevent hydrate formation in measuring and regulating equipment, certain precautions have to be taken. It is possible to avoid down time and a lot of operational problems by proper design and handling procedures in gas production e.g. avoiding unnecessary pressure and temperature drops, insulation of piping to keep gas temperature above hydrate zone, providing isolation and blowdown valves with points for methanol injection etc.

It is possible to predict change in conditions of hydrate formation and hydrate prevention from generalized graphs showing effect of pressure and inhibitor solution concentration on the hydrate formation conditions for different gases (Makagon, 1981). For gases of different compositions at different pressures, it is found that the hydrate formation temperature is lowered by different amounts by injecting an inhibitor solution of a specified concentration.

Koledzinski and Arshinov (1970) have discussed the method of hydrate inhibitor injection in the bottom hole well bore vicinity at Messoyakha field. They suggested that 30% calcium chloride solution be used as inhibitor in summer and a mixture of methanol and calcium chloride in winter, the quantity of inhibitor being calculated taking into consideration the capacity of the casing. A cyclic procedure of inhibitor injection, followed by oil production is followed, where the frequency of inhibitor injection can be determined by field experimentation. They also suggested that if hydrates existed in well bore hole, it was necessary to inject inhibitor continuously

to avoid formation of hydrates.

14. Environmental Problems due to Hydrate Formation & Dissociation

If hydrates are present in conjunction with oil or free gas, although they provide a potential source of free gas, they also affect the produceability of the crude oil or natural gas reservoir. The formation of gas hydrates in oil and gas reservoirs drastically reduces the permeability of the reservoir to oil and gas flow.

In addition, a crude oil may be denuded of its lighter components, due to formation of hydrates. This not only increases the viscosity of the oil but also reduces the efficiency of the recovery processes. (Holder et al, 1976, Verma et al, 1974). Also, it has been reported that there have been gas blowouts in coal mines due to accumulation and decomposition of gas hydrates in porous media, (Makogen, 1978).

Topham (1984 a,b) has reported that the formation of hydrates in deep sea environment may result in an oil well blowout due to channelling of gas in the form of hydrated plumes of hydrocarbon gases. This reduces the buoyancy of the otherwise fast rising bubble plumes, thereby causing extensive damage.

Recently, Godbole et al (1987) have analysed the hydrate formation and dissociation from bubble plumes rising in deep sea waters. The zones of hydrate formations in deep waters have been determined for various potential arctic offshore exploration areas. A new hydrodynamic model for the hydrate forming bubble plumes has been developed which includes spherical as well as elliptical bubble shapes with appropriate drag coefficients. The model also addresses the ultimate fate of the oil after the hydrated plume dissociates back into gas.

Apart from these there are other problems due to hydrate formation or dissociation in the reservoir or near well bore.

Hydrate dissociation can cause soil compaction due to phenomena similar to thaw subsidence in permafrost.

Hydrate formation can cause freeze back pressure phenomena and cause damages to the well bore.

15. OTHER USES OF HYDRATES

One of the principal areas in which hydrates can be potentially used is in the desalination of sea water (Knox et al, 1961, Barduhn et al, 1962). In this approach, pure water is separated from its solution in a solid form by reacting with hydrating agents like propane, methyl bromide, Freon 22 etc, to form a gas hydrate. As hydrates are stable above 0°C, refrigeration costs can be reduced in processes that use freezing methods to desalinate sea water.

Gas hydrates can be used as a form of underground storage of natural gas (Parent, 1968), who found that the storage of natural gas as a solid was more safer than as liquid. Child (1964) suggested that hydrates can be used in transporting and storing radioactive gases such as Krypton, which itself is capable of forming hydrates. Makagon (1974) suggested that hydrates could be used as gas blowout preventer in coal mines as well as in fog and cloud dispersion.

16 NOMENCLATURE

a	Kihara Special Core Radius
b	Structure dependent parameter for specific heat
C_{ij}	Langmuir constant for an ith molecule in a jth cavity
L₁	Water rich liquid phase
L₂	Hydrocarbon rich liquid phase
M	Hydrocarbon gas M
N	Integer Constant
n	Hydrate number
P	Dissociation pressure, kPa or psi
R	Gas Constant, Joule/mole.K
R_j	Radius of cavity j
r	radial distance from centre of cavity
T	temperature, °C or °K
V	Vapour phase
f	gas phase - fugacity
W_{ij}	smoothed cell potential function
V_j	ratio of number of j cavities to the number of water molecules in hydrate phase
I	rate of formation of nuclei
D_w	diffusivity of water through hydrate film
V_T	radial growth rate of surface film hydrate
M_w	water diffusion rate
D_w	Diffusivity of water through hydrate film
STP	Standard Temperature and Pressure
a_s	interfacial area

Greek Letters

Δ	indicates difference in property
ϵ	gas-water Kihara energy parameter, joule/molecule
μ	chemical potential of water, joule/mole
σ	Kihara distance parameter, pm
θ	Fractional occupancy of the cavity
ω	Accentric factor of gas molecule
τ	Hydrate growth time
γ	overall order of reaction w.r.t. pressure
χ	absolute activities
ζ	density in hydrate phase

Subscripts

1	In pure water
2	in aqueous solution
g	gas phase
h	Hydrate Phase
i	Gas Species, i
j	Cavity type j
liq	liquid phase
$solid$	solid (ice) phase
w	water or ice phase
B	unoccupied water phase

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SECTION III

HYDRATE DISSOCIATION MODELLING AND IMPLICATIONS OF HYDRATE DISSOCIATION DURING DRILLING IN ARCTIC OFFSHORE AND ONSHORE ENVIRONMENTS

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1.0 IMPLICATIONS OF DISSOCIATION OF IN-SITU GAS HYDRATE DEPOSITS

1.1 Introduction

The presence of natural gas hydrates in arctic and subsea regions is well documented. Hydrate cores have been obtained from the Gulf of Mexico, the western coast of Guatemala, and in 1972, ARCO and EXXON recovered a hydrate core sample near Prudhoe Bay, Alaska. In addition, hydrate deposits in the Canadian and Russian Arctic are known to exist (Bily and Dick, 1974; Makogon, 1965).

Gas hydrates are crystalline compounds (clathrates) of gas and water, which are formed at relatively low temperatures and high pressures. These hydrates occupy much less volume than the unhydrated natural gas and water. One hundred percent methane saturated hydrates can contain up to 181.3 standard cubic feet of methane in hydrated form in just one cubic foot of pure hydrate. It is because of this concentrated form that natural gas hydrates have generated such interest as a potential future energy source, and that precautions must be taken when drilling through hydrate bearing formations.

1.2 Drilling Problems

Drilling through hydrate formation can cause well control problems due to severe mud gasifications if proper drilling procedures are not followed. Sizeable gas kicks and potential blowout conditions have been reported in the literature (Davidson et al, 1978; Franklin, 1979). Problems of well control due to severe mud gasification were reported by Imperial Oil Ltd. (Bily

and Dick, 1974), and Panarctic Oils Ltd. (Franklin, 1979). Other hydrate experiences include fizzed drill cuttings and wellbore freeze-up and casing collapse (Makogon, 1965; Franklin, 1979).

During drilling through a naturally occurring hydrate zone, hydrates are exposed to an increased temperature which causes dissociation of hydrates into gas and water, providing gas influx into the wellbore. This gas reduces the hydrostatic pressure of the mud column, further accelerating the hydrate dissociation in the vicinity of the wellbore. If the dissociation is rapid and significant, it can introduce a large gas influx from the dissociated hydrate zone into the wellbore causing a gas kick. The gas kick control problem has been discussed by Nickens (1985) and Ekran and Rommetveit (1985).

Several specific examples of drilling problems encountered while drilling through hydrate zones have been discussed by Franklin (1979). The two most notable examples he reports are for wells drilled at Mearne Point on Mellville Island and in Jackson Bay. Problems encountered in the Mearne Point well included: a 22 percent gas cut at 356 meters (1,168 ft.); drill stem tools became frozen in the hole at the same depth; a sizeable gas kick occurred at 895 meters (2,936 ft.); hole stability problems were encountered at a depth of 1,676 meters (5,499 ft.); and while logging at a depth of 1,676 meters, a gas kick occurred and the logging tools were lost down the hole.

Incidents reported at the Jackson Bay well were just as significant. A 50 barrel kick was taken at a depth of 1,715 feet. Gas flow after each connection to a depth of 4,000 feet

resulted in the loss of about 5 barrels of mud per connection. At a depth of 4,000 feet, three days of circulation with increased mud density (14 lb/gal) were required to sufficiently stabilize the hole for the running of casing. In drilling below this depth, a background gas cut of 1 to 5 percent was noted while drilling, and a gas cut of 10 to 12 percent was recorded on connections.

Currently, two different methods are used to drill through hydrate containing formations. Predominately, cool drilling fluid with higher mud weight at high circulation rates is used to slow or prevent hydrate dissociation in the formation. Panarctic Oils Ltd., alternatively, tried to promote the dissociation at early times while the drill pipe is in the hole by using low weight muds with proper degassing equipment at the surface (Franklin, 1980).

1.3 Production of Natural Gas From Hydrates

The amount of natural gas bound in hydrate form has been estimated to be in excess of 10^{20} standard cubic feet, an overwhelming quantity when you consider the world's conventional gas resources are estimated to be 2.9×10^{15} standard cubic feet. Because the solid hydrates are immobile and relatively impermeable, they need to be dissociated into gas and water in order to produce natural gas from the reservoir in a conventional gas well.

The stability of natural gas hydrates is a function of three variables, namely pressure, temperature, and reservoir brine

salinity. Dissociating hydrates into gas and water required that one of these three parameters be altered in such a fashion as to destabilize the hydrates. There have been several methods suggested in the literature (McGuire, 1981; Holder et al, 1982; Holder and Angert, 1982; Bayles et al, 1984; Kamath and Godbole, 1985; Selim and Sloan, 1985). These include thermal recovery techniques such as steam injection or stimulation, hot water injection and fire flooding, depressurization, and injection of chemicals such as methanol or glycol which cause hydrate destabilization.

Holder et al (1982) showed that thermal recovery techniques are energy efficient from a thermodynamic standpoint, i.e., the heat required to dissociate hydrates is only a small fraction (about one tenth) of the heat that is obtained by burning the gas produced from the hydrates. Of the thermal recovery methods suggested, each has its own merits and demerits. In steam injection and fire flooding, heat losses could be severe for thin hydrate zones, but could be thermally efficient for thicker zones (greater than 50 feet). Fire flooding could cause dilution of the the gas produced and thereby reduce its energy value. Hot water injection will yield lower heat losses, but injectivity of water into the hydrate reservoir will govern the applicability of the method. The injection water temperature should be low enough to avoid excessive heat losses, yet high enough to avoid unrealistically high injection rates. Hydraulic fracturing could be employed to improve water injectivity, but could result in lower heat transfer efficiencies due to channeling effects.

In 1984, Bayles et al presented a steam cycling model gas production from a hydrate reservoir. They found gas production to vary from 2.5 to 110 million standard cubic feet per year for a variety of reservoirs. The energy efficiency ranged from a low of 4.0 to a high of 9.6 combustible energy of the produced gas to the energy of the injected steam.

Selim and Sloan (1985) presented a model for dissociation of pure hydrates and found the energy efficiency to be 13, which is close to the thermodynamic efficiency. This should have been expected since their model does not consider heat losses or a porous rock matrix structure containing the hydrates.

Also in 1985, Kamath and Godbole presented a hot brine stimulation model for gas production from natural gas hydrates. For a 100 foot thick hydrate reservoir, they found an overall energy efficiency ratio of approximately 9 to 13 after 1,000 days for various brine salinities. Their study also concluded that brine injection resulted in higher thermal efficiencies and therefore higher gas production than steam for the same heat injection rate. This conclusion is, however, based on the assumption that the dissociated zone volume was capable of handling the predetermined injection rate of hot water.

Holder and Angert (1982) studied the depressurization scheme of dissociating hydrates. In this method, the sensible heat of the reservoir provides the energy necessary for hydrate dissociation. In this method, the gas pressure adjacent to the solid hydrate must be reduced. The hydrates, which produce their own vapor pressure, will dissociate until their vapor pressure is

reattained. In doing this, the hydrates exhibit a Joule-Thompson effect, becoming colder as they dissociate. A temperature gradient is thus generated between the hydrates and the surrounding formation and heat must flow to the hydrates. By keeping the pressure low by removing gas, the hydrates continue to dissociate, remaining colder than the surrounding media, thus maintaining the temperature gradient and heat flux to the hydrates. In their study, a hydrate layer was assumed to exist in association with a conventional gas layer. They found that the hydrates may account for up to 30 percent of the total gas production under this scheme.

Use of hydrate inhibitors such as methanol or glycol has not been studied in detail, but it may be safe to assume that their use would be governed by economics since large quantities of these relatively expensive chemicals may be required to ensure sufficient gas production.

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2.0 MATHEMATICAL MODEL FOR DRILLING IN THE PRESENCE OF HYDRATES

2.1 Introduction

The two-dimensional transient heat transfer model developed in this study couples the hydraulics and heat transfer in the wellbore with hydrate dissociation (and/or permafrost thaw) for both arctic and subsea locations. This model was derived from the wellbore heat transfer models of Keller et al (1973) and Marshall and Bentsen (1982) and the development of a fundamental hydrate dissociation model.

2.1 Model Considerations and Assumptions

Figure 1 represents the physical model on which the computer model is based for arctic regions. The model includes options for a full well completion scheme with any number of casing strings, or a simplified version which neglects the well completion and assumes a uniform hydraulic radius. For subsea locations, an option is included which either allows or neglects a riser casing to the platform.

The assumptions incorporated in this model for the drilling fluid and wellbore region include:

1. Heat transfer within the drilling fluid is by axial convection. Conduction is negligible except when circulation is stopped.

Figure 1: Schematic Diagram of a Well for the Arctic Region

2. Radial temperature gradients within the drilling fluid are negligible.
3. Radial conduction in the drill pipe wall is negligible compared to the radial convection between the drilling fluid and pipe wall.
4. Heat generation by viscous dissipation within the drilling fluid is negligible.
5. Fluid properties, i.e. density, thermal conductivity, and heat capacity, are independent of temperature.

Within the formation, there are five distinct zones that need to be accounted for: thawed permafrost region, unthawed permafrost region, solid formation, dissociated hydrate region, and solid hydrate region. The assumptions incorporated into the model for these five zones include:

6. Effects beyond the outer boundaries of the system are negligible.
7. There are no heat sources or sinks.
8. Each zone is individually homogeneous and isotropic.
9. Heat transfer in each region is by conduction only.
10. The thermophysical properties of each zone, i.e. thermal conductivity, heat capacity, and density, are constant within each zone and different across the boundaries separating each zone.
11. The formation above and below the hydrate zone is impermeable.
12. The gas produced from the dissociation of hydrates migrates rapidly to the well.

13. The hydrate zone is completely saturated with methane hydrates.

2.3 Model Equations

Five partial differential equations may be written to describe energy balances within the system. The heat flow within the drill string is described by Equation (1).

$$\begin{aligned}
 & 8.021 \rho_m C_{p_m} q_m \frac{\partial T_p}{\partial z} + 2\pi r_{pi} h_{pi} (T_{pi} - T_w) \\
 & = - \rho_m C_{p_m} \pi r_{pi}^2 \frac{\partial T_p}{\partial t} + Q_{pi}
 \end{aligned} \tag{1}$$

The terms on the left represent the vertical and radial heat convection, respectively. The energy accumulation and source terms are represented by the right side terms, respectively.

Equation (2) represents the energy balance in the drill pipe wall.

$$\begin{aligned}
 & k_w \frac{\partial^2 T_w}{\partial z^2} + \frac{2r_{pi} h_{pi}}{(r_{po}^2 - r_{pi}^2)} (T_{pi} - T_w) \\
 & + \frac{2r_{po} h_{po}}{(r_{po}^2 - r_{pi}^2)} (T_a - T_w) \\
 & = \rho_w C_{p_w} \frac{\partial T_w}{\partial t}
 \end{aligned} \tag{2}$$

The right-hand term is the heat accumulation within the wall. The left side terms represent, respectively, vertical heat

conduction within the wall, radial heat transfer to (from) the pipe wall from (to) the fluid inside the drill pipe, and radial heat transfer from (to) the pipe wall to (from) the annulus fluid.

The energy balance in the flow annulus is given by Equation (3).

$$\begin{aligned}
 & 8.021 \rho_{\text{meq}} C_{p_{\text{meq}}} q_m \frac{\partial T_a}{\partial z} + 2\pi r_{\text{po}} h_{\text{po}} (T_w - T_a) \\
 & + \rho \pi r_{\text{wb}} h_{\text{wb}} (T_k - T_a) \\
 & = \rho_{\text{meq}} C_{p_{\text{meq}}} (r_{\text{wb}}^2 - r_{\text{po}}^2) \frac{\partial T_a}{\partial t} - Q_a, \\
 & k = c, \text{ for, Dp, DH}
 \end{aligned} \tag{3}$$

The left-hand terms include the vertical heat convection within the fluid, radial convection between the pipe wall and annulus fluid, and radial convection between the annulus fluid and the formation (or casing). On the right-hand side are the energy accumulation term and the energy source term, respectively.

Equation (4) expresses the energy balance in the first grid inside the formation or casing.

$$\begin{aligned}
 & \frac{\partial^2 T_k}{\partial z^2} + \frac{1}{r} \frac{\partial T_k}{\partial r} + \frac{\partial^2 T_k}{\partial r^2} \\
 & + \frac{2r_{\text{wb}} h_{\text{wb}} (T_a - T_k)}{k_k \left[\left(\frac{r_1 + r_1 + 1}{2} \right)^2 - r_{\text{wb}}^2 \right]}
 \end{aligned} \tag{4}$$

$$= \frac{1}{\alpha_k} \frac{\partial T_k}{\partial t}, \quad k = c, \text{ for, } Dp, Dh$$

The left-hand terms are the vertical and radial conduction terms and the radial convection between the annulus fluid and the formation, respectively. The energy accumulation term appears on the right-hand side. The subscript on the thermophysical properties indicates that this equation, depending on the completion scheme and depth location, may be applied to four different materials or zones, i.e., casing, thawed permafrost, solid formation, or dissociated hydrate region.

The final equation represents the energy balance elsewhere within the completion scheme or formation.

$$\frac{\partial^2 T}{\partial z^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} = \frac{1}{\alpha_k} \frac{\partial T}{\partial t}, \quad (5)$$

$$k = c, c_e, Dp, Sp, \text{ for, } DH, SH$$

This equation is the well known two-dimensional cylindrical coordinate heat conduction equation. The subscript on the thermal diffusivity indicates that this equation may be applied to seven different materials, i.e., casing, casing annular material (cement), thawed permafrost, unthawed permafrost, solid formation, dissociated hydrate region, and solid hydrate regions.

In order to solve these equations we need the boundary conditions, the wellbore hydraulics, a means of determining the convective heat transfer coefficients for the particular fluid

rheology and flow regime, i.e. turbulent or laminar, and the energy source terms within the wellbore region. Due to the limited space available, the wellbore hydraulics will not be presented here, but rather, referenced as being the same as presented in Bourgoyne et al (1986) for Newtonian fluids, Bingham plastics, and power law fluids. The correlations for determining the convective heat transfer coefficients and the method of evaluating the energy source terms are presented in Appendix A.

The appropriate initial and boundary conditions are described below. The initial condition describes the initial temperature profile as being the geothermal gradient:

$$T_{i,j}^0 = T_{ms} + \varepsilon_G z_j \quad (6)$$

The upper and lower boundary conditions are respectively:

$$\frac{\partial T}{\partial z} = 0, \quad z = 0 \quad (7)$$

$$T_{i,j_{max}+1}^n = T_{i,j_{max}+1}^0 \quad (8)$$

The inner and outer radial boundary conditions indicate no heat flow across these boundaries:

$$\frac{\partial T}{\partial r} = 0, \quad r = 0 \quad (9)$$

$$\frac{\partial T}{\partial r} = 0, \quad r = r_e \quad (10)$$

The innermost upper grid temperature is defined as the fluid inlet temperature:

$$T_{1,0}^n = T_{m1} \quad (11)$$

Equation (12) expresses the requirement that the temperatures be equal at the drill bit depth within the wellbore:

$$T_{1,jmax}^n = T_{2,jmax}^n = T_{3,jmax}^n \quad (12)$$

Because thawing of permafrost and dissociation of hydrates represent moving boundary problems, boundary conditions at the moving boundaries separating the thawed and unthawed permafrost regions and the dissociated and undissociated hydrate regions are required. These boundary conditions are of the same form for either permafrost or hydrates and so indicated by subscripts for each region. For the permafrost region, the first moving boundary condition expresses the requirement that the boundary be an isotherm:

$$T_{Dp}(r_{fp}, z_{fp}, t) = T_{Sp}(r_{fp}, z_{fp}, t) = T_{fp} \quad (13)$$

This is not true for the hydrate moving boundary as it is a strong function of pressure and therefore vertical position:

$$T_{DH}(r_{fH}, z_{fH}, t) = T_{SH}(r_{fH}, z_{fH}, t) = T_{fH}(z_{fH}) \quad (14)$$

The second set of moving boundary conditions are identical in form and express the requirement that the heat flux entering the boundary less the heat flux leaving the boundary be equal to the amount of permafrost thawed or hydrate dissociated:

$$\begin{aligned} & \left\{ 1 + \left[\frac{\partial s(z,t)}{\partial z} \right]^2 \right\} \left[k_{Sk} \frac{\partial T_{Sk}(r,z,t)}{\partial r} \right. \\ & \left. - k_{Dk} \frac{\partial T_{Dk}(r,z,t)}{\partial r} \right] = -\rho_k L_{fk}(z) \frac{\partial r_{fk}}{\partial t}, \end{aligned} \quad (15)$$

$k = p, H$

$$\begin{aligned} & \left\{ 1 + \left[\frac{\partial s(r,t)}{\partial r} \right]^2 \right\} \left[k_{Sk} \frac{\partial T_{Sk}(r,z,t)}{\partial z} \right. \\ & \left. - k_{Dk} \frac{\partial T_{Dk}(r,z,t)}{\partial z} \right] = -\rho_k L_{fk}(z) \frac{\partial z_{fk}}{\partial t}, \quad k = p, H \end{aligned} \quad (16)$$

Equations (15) and (16) express the rate of front advance in the radial and vertical directions, respectively.

The data utilized in this study are included in Tables 1 and 3.

The partial differential equations are written in a fully implicit finite difference form and the temperature distributions are solved by a direct solution method involving the LU decomposition approach. The solution of the wellbore hydraulics and heat transfer model indicated that the thermal gradient in the vertical direction in the wellbore for the thickness of the hydrate zone is not significant. Therefore, we assumed a constant temperature front in the wellbore and analyzed the decoupled hydrate dissociate model. The dimensionless form of fundamental hydrate dissociation model is discussed in detail.

TABLE 1

Wellbore, Drilling Fluid and Reservoir Parameters

ρ_{for}	=	167 (lb/ft ³)
Cp_{for}	=	.2 (Btu/lb °F)
k_{for}	=	1.36 (Btu/hr ft °F)
ρ_{wat}	=	62.4 (lb/ft ³)
Cp_{wat}	=	1.08 (Btu/lb °F)
k_{wat}	=	0.343 (Btu/hr ft °F)
Cp_{C1}	=	0.5 (Btu/lb °F)
k_{C1}	=	0.0178 (Btu/ft hr °F)
ρ_h	=	57.1 (lb/ft ³)
Cp_H	=	0.54 (Btu/lb °F)
k_H	=	0.2274 (Btu/lb °F)
β_H	=	181.3 (SCF/ft ³ hydrate)
S_H	=	1.0
S_g	=	0.2
S_{wat}	=	0.8
r_e	=	0.8
A_{bit}	=	0.451 (ft ²)
k_m	=	1.0 (Btu/ft hr °F)
Cp_m	=	0.4 (Btu/lb °F)
ρ_w	=	486.0 (lb/ft ³)
k_w	=	25.28 (Btu/ft hr °F)

TABLE 2

Key Process Parameters

<u>Parameter</u>	<u>Range</u>
Wellbore Diameter, D_{wb}	6-12 (inches)
Hydrate Zone Thickness, H_{Hyd}	20-150 (feet)
Mud Density, ρ_m	10-18 (lb/gal)
Mud Viscosity, μ_m	20-100 (cp)
Mud Circulation Rate, q_m	100-500 (gal/min)
Bottom-Hole Mud Temperature, T_m	40-120 ($^{\circ}F$)
Geothermal Gradient, ξ_G	0.01-0.05 ($^{\circ}F/ft$)
Sea Depth, z_{sea}	1,000-8,000 (ft)
Mud Inlet Temperature, T_{mi}	50-120 ($^{\circ}F$)

TABLE 3

Base Case Model Parameters

D_{pi}	=	5.921 (in)
D_{po}	=	6.625 (in)
D_{wb}	=	8.375 (in)
ρ_m	=	10.0 (lb/gal)
μ_m	=	45.0 (cp)
q_m	=	200 (gal/min)
ϕ	=	0.2
H_{Hyd}	=	20 (ft)
z_{Hyd}	=	3,500 (ft)
z_{pfb}	=	2,500 (ft)
ξ_G	=	0.01 ($^{\circ}F/ft$)
T_{ms}	=	10 ($^{\circ}F$)
ω	=	350 (rpm)
τ	=	1875.8 (ft-lbf/min)
Q_p	=	20 (ft/hr)
T_{MBH}	=	80 ($^{\circ}F$)

2.4 Fundamental Hydrate Dissociation Model

2.4.1 Dimensionless Variables

The spatial coordinates are normalized as

$$u = \ln (r/r_w) / \ln (r_e/r_w), \quad r_w < r < r_e \quad (17)$$

and

$$v = z/H, \quad 0 < z < H \quad (18)$$

Two advantages realized from these transformations are:

1. When u is discretized, the closely spaced grid points result near the inner boundary where the solution changes rapidly, and
2. the rectangular domain $(r_w < r < r_e)$ and $(0 < z < H)$ is mapped to a square in the region $(0 < u < 1)$ and $(0 < v < 1)$.

Prior to defining a dimensionless time, the thermal diffusivities of each zone are determined.

Hydrate Zone:

$$(\rho C_p)_H = (1-\phi) \rho_R C_{pR} + \phi \rho_H C_{pH} \quad (19)$$

$$K_H = K_R \left[\frac{\phi^{2/3} (\delta_H - 1) + 1}{(\delta_H - 1)(\phi^{2/3} - \phi) + 1} \right] \quad (20)$$

where

$$\delta_H = K_H/K_R \quad (21)$$

$$D_H = K_H/(\rho C_p)_H$$

Dissociated Zone:

$$(\rho C_p)_D = (1-\phi) \rho_R C_{pR} + \phi(\rho_w C_{pw} S_w + \rho_g C_{pg} S_g) \quad (22)$$

The gas density used here is calculated as

$$\rho_g = 2.7 \frac{\gamma_g P_R(Z)}{Z_g T_f(Z)} \quad (23)$$

where $P_R(Z)$ is the hydrostatic pressure at the hydrate depth,

$$P_R(Z) = 0.435Z + 14.7 \quad (24)$$

and $T_f(Z)$ is the hydrate dissociation temperature (methane hydrates),

$$T_f(Z) = \frac{15360.8}{37.05 - \ln(P_R(Z))} - 459.7 + a_{fx} \quad (25)$$

The gas compressibility factor is calculated using the Standing modification of the Brill and Beggs correlation for curve fitting the Standing-Katz z-factor charts (Standing, 1977).

$$K_D = K_R \left[\frac{S_w \{ \phi^{2/3} (\delta_w - 1) + 1 \}}{(\delta_w - 1) (\phi^{2/3} - \phi) + 1} + \frac{S_g \{ \phi^{2/3} (\delta_g - 1) + 1 \}}{(\delta_g - 1) (\phi^{2/3} - \phi) - 1} \right] \quad (26)$$

Where $\delta_w = K_w/K_R$ and $\delta_g = K_g/K_R$.

$$D_D = K_D / (\rho C_p)_D \quad (27)$$

Dimensionless time (Fourier's number) can now be defined for each region, i.e. dissociated hydrate zone, solid hydrate zone, and the overburden and underburden:

$$\tau_{D_i} = D_i t / r_w^2, \quad i = D, S, O \quad (28)$$

Dimensionless temperatures are defined by

$$\theta_i(u, v, \tau_{D_i}) = \frac{[T(u, v, \tau_{D_i}) - T_f(v)]}{[T_w - T_f(v)]} \quad (29)$$

where, $i = D, S, O$

and $T_f(v)$ is given by Equations (24) and (25).

The following dimensionless terms are also defined:

$$\beta = r_e / r_w \quad (30)$$

$$\lambda = [\ln(r_e / r_w)]^2 \quad (31)$$

$$\mu = (r_w/H)^2 \quad (32)$$

$$\begin{aligned} \epsilon(v) = & \frac{T_f^2(v)}{15360.8 H [T_w - T_f(v)]} \\ & \times \left[\frac{0.435}{0.435(Z - vH) + 14.7} \right] \end{aligned} \quad (33)$$

$$\begin{aligned} \sigma(v) = & \left[\frac{0.435}{0.435(Z - vH) + 14.7} \right]^2 \\ & \times \left[\frac{T_f^2(v)}{15360.8 H^2 [T_w - T_f(v)]} \right] \\ & \times \left[\frac{2T_f(v)}{15360.8} - 1 \right] \end{aligned} \quad (34)$$

2.4.2 Dimensionless Differential Equations and Boundary Conditions

The dimensionless differential equation describing unsteady-state heat conduction in an isotropic medium can now be expressed as

$$\begin{aligned} & \frac{\beta}{\lambda} \frac{\partial^2 \theta_1(u, v, \tau_{D1})}{\partial u^2} + \mu \frac{\partial^2 \theta_1(u, v, \tau_{D1})}{\partial v^2} \\ & - 2\mu\epsilon(v) \frac{\partial \theta_1(u, v, \tau_{D1})}{\partial v} \end{aligned}$$

$$+ \mu \sigma(v)[1 - \theta_i(u, v, \tau_D)] = \frac{\partial \theta_i(u, v, \tau_D)}{\partial \tau_{D_i}} \quad (35)$$

where, $i = D, S, 0$

Initial Condition

$$\theta_i(u, v, 0) = \frac{[T_{in}(v) - T_f(v)]}{[T_w - T_f(v)]} \quad (36)$$

$$0 < u < 1, 0 < v < 1, \tau_{D_i} = 0, i = S, 0$$

where,

$$T_{in}(v) = (Z - vH - Z_{pfb}) G_{th} + 30.2 \quad (37)$$

and

$$Z_{pfb} = (30.2 - T_{ms})/G_{fr} \quad (38)$$

Inner Boundary Condition

$$\theta_i(0, v, \tau_{D_i}) = 1,$$

$$u = 0, 0 < v < 1, \tau_{D_i} > 0, i = D, 0 \quad (39)$$

Outer Boundary Condition

$$\theta_i(1, v, \tau_{D_i}) = \frac{[T_{in}(v) - T_f(v)]}{[T_w - T_f(L)]} \quad (40)$$

$$u = 1, 0 < v < 1, \tau_{D_i} > 0, i = S, 0$$

Upper and Lower Boundary Conditions

$$\frac{\beta}{\lambda} \frac{\partial^2 \theta_0(u, v, \tau_{D_0})}{\partial u^2} = \frac{\partial \theta_0(u, v, \tau_{D_0})}{\partial \tau_{D_0}} \quad (41)$$

$$0 < u < 1, v = 1, \tau_{D_0} > 0$$

$$\frac{\beta}{\lambda} \frac{\partial^2 \theta_0(u, v, \tau_{D_0})}{\partial u^2} = \frac{\partial \theta_0(u, v, \tau_{D_0})}{\partial \tau_{D_0}} \quad (42)$$

$$0 < u < 1, v = 0, \tau_{D_0} > 0$$

Moving Boundary Conditions

1. From temperature continuity considerations,

$$\theta_D(u_f, v_f, \tau_{D_D}) = \theta_S(u_f, v_f, \tau_{D_S}) = \theta_f \quad (43)$$

Where u_f and v_f are the coordinates of any given point on the moving boundary.

2. From the energy balance considerations at the moving boundary,

the Stefan conditions are:

$$\begin{aligned} & [1 + \mu \lambda \beta^{2u} (\frac{du_f}{dv})^2] [\frac{K_S}{K_D} \frac{\beta^{-2u}}{\lambda} \frac{\partial \theta_S(u, v, \tau_{D_S})}{\partial u} \\ & - \frac{\beta^{-2u}}{\lambda} \frac{\partial \theta_D(u, v, \tau_{D_D})}{\partial u}] = \frac{L_f(v)}{C_{pD} [T_w - T_f(v)]} \frac{du_f}{d\tau_{D_D}} \end{aligned} \quad (44)$$

and

$$\begin{aligned} & [1 - \frac{\beta^{-2u}}{\mu \lambda} (\frac{dv_f}{du})^2] [\frac{K_S}{K_D} \{ \frac{\partial \theta_S(u, v, \tau_{D_S})}{\partial v} + \varepsilon(v) \} - \\ & \{ \frac{\partial \theta_D(u, v, \tau_{D_D})}{\partial v} + \varepsilon(v) \}] \\ & = \frac{L_f(v)}{C_{pD} \mu [T_w - T_f(v)]} \frac{dv_f}{d\tau_{D_D}} \end{aligned} \quad (45)$$

where $L_f(v)$ is the latent heat of fusion of the hydrates and is determined by

$$L_f(v) = \phi S_H [10743.1 - 1.9204 T_f(v)] \quad (46)$$

2.4.3 General Solution Method of the Fundamental Hydrate Dissociation Model

The solution of the above problem involves determination of the temperature distribution in each zone and the position of the

moving boundary at any time τ_{Dn} , $n = 0, 1, 2, \dots, N-1$.

In general, it is necessary to solve four separate problems to obtain the solution at time τ_{Dn+1} for the time interval $\Delta\tau_{Dn}$. The first three problems are boundary value problems, the solutions of which give the temperature distribution in each of the zones. The fourth problem consists of two sets of initial value problems, the solutions of which give two sets of vectors $\vec{u}_{fp}$, $p = 1, 2, \dots, P$ and $\vec{u}_{fq}$, $q = 1, 2, \dots, Q$ defining the position of the moving boundary. Here P is the number of grid points that the interface intersects grid lines parallel to the u coordinate and Q those parallel to the v coordinate.

The boundary value problems, given in dimensionless form by equations (35) through (43) and written for each zone, are solved using an iterative, semi-implicit line successive over-relaxation technique (LSOR) (Crichlow, 1977). In applying this technique to a particular grid line in the hydrate zone, the temperature distribution is determined first for the dissociated zone, followed by the solid hydrate zone, and then the temperatures along the whole grid line are relaxed.

The two sets of initial value problems given in dimensionless form by equations (44) and (45) are solved by the trapezoidal method.

To advance the solution from τ_{Dn} to τ_{Dn+1} , the algorithm presented by Sengul (1977) is used with slight modification. The major difficulty in obtaining a solution is the evaluation of the initial value problems because it requires an estimation of the temperature gradients at the moving boundary. To evaluate these

temperature gradients, the temperatures of the grid points on either side of the interface and the temperature of the moving boundary are fitted to a polynomial using a least squares method (Gerald and Wheatly, 1984). The degree of polynomial fit to the temperature profiles is allowed to vary from degree 1 to degree 9. The optimum degree of the polynomial is selected by increasing the degree of the polynomial, beginning with degree one, so long as there is a significant decrease in the variance (Gerald and Wheatly, 1984).

Once these polynomials have been determined for the temperature profiles in each of the dissociated and solid hydrate zones in the u direction and in the v direction, Richardson Extrapolation (Cheney and Kincaid, 1985) is used to determine the first derivative of the polynomials, i.e. the temperature gradients at the moving boundary. The details of the solution method are discussed elsewhere (Roadifer, 1987).

2.4.4 Gas Influx Calculations

Once the above problem has been solved for some time period, Δt , a simple material balance is used to calculate the gas influx into the wellbore.

The volume of hydrate dissociated is given by

$$V_H = \pi \phi H_H \{ [r_f(t + \Delta t)]^2 - [r_f(t)]^2 \} \quad (47)$$

The moles of methane gas originally contained in this volume is

$$n_{gH} = \frac{181.3}{379.5} V_H \quad (48)$$

The moles of methane gas the dissociation volume would contain at wellbore conditions is

$$n_{gWB} = \frac{P_F V_H S_g}{z_g R T_m} \quad (49)$$

2.5 Summary and Conclusions

A comprehensive wellbore hydraulics and heat transfer model and a fundamental hydrate dissociation model has been developed. The model development allows the detailed examination of the effects of a wide range of drilling parameters on the wellbore pressure, wellbore temperature and, consequently, hydrate dissociation rate for arctic terrestrial, arctic subsea and subtropic subsea locations.

2.6 NOMENCLATURE

a_{fx}	=	freezing point depression of hydrates due to dissolved solids
C_p	=	specific heat (Btu/lb [°] F)
D	=	diameter (inches) or thermal diffusivity (ft ² /hr)
E_{fr}	=	frictional energy losses (Btu/ft hr)
E_{rot}	=	rotational energy (Btu/ft hr)
f	=	positin of the interface
g_G	=	geothermal gradient (°F/ft)
G_{fr}	=	geothermal gradient within permafrost (°F/100 ft)
G_{th}	=	geothermal gradient below permafrost (°F/100 ft)
h	=	convective heat transfer coefficient (Btu/hr [°] F ft ²)
H	=	zone thickness (feet)
k	=	thermal conductivity (Btu/ft hr [°] F)
L_f	=	latent heat (Btu/lb)
M	=	number of space intervals in both the u and v directions
MU	=	number of grids in the underburden in the v direction
N	=	total number of time steps
N_{Re}	=	Reynold's number
N_{Nu}	=	Nusselt number
p	=	number of intersections of the moving boundary with grid lines parallel to the u coordinate
P	=	pressure (psia)
P_r	=	Prandtl number
ppr	=	natural log of pressure
q	=	flow rate (gal/min)
Q	=	heat energy source term (Btu/ft hr)
Q	=	gas influx rate (scf/min)

Q = number of intersections of the moving boundary with grid lines parallel to the v coordinate
 QP = formation penetration rate (ft/hr)
 r = radius (feet)
 r_e = radius to the outer boundary
 r_f = radius to the moving boundary (front)
 r_n = dimensionless variable defined as $\Delta\tau_D/(\Delta u)^2 = \Delta\tau_D/(\Delta u)^2$
 s = wellbore radius
 S = Surface
 St = Stanton number
 t = time (hours)
 T = temperature (°F)
 T_{bpf} = temperature at the base of the permafrost
 T_{in} = initial temperature distribution
 u = normalized radial direction
 u_f = dimensionless radial position of the moving boundary
 v = normalized vertical direction
 V = Volume
 V = velocity (ft/s)
 v_f = dimensionless vertical position of the moving boundary (below inflection point)
 z = depth (ft.)

Greek Symbols

α = thermal diffusivity (ft²/hr)
 α = curvilinear coordinate transformation variable
 β = hydrate gas content (SCF/ft³ hydrate)

β = dimensionless variable defined in Equation 30
 γ = curvilinear coordinate transformation variable
 ϵ = dimensionless variable defined by Equation 33
 θ = 1. angle
 = 2. dimensionless temperature
 λ = dimensionless variable defined by Equation 39
 σ = dimensionless variable defined by Equation 41
 ρ = density (lb/ft³)
 μ = viscosity (cp)
 ϕ = porosity
 τ = dimensionless time (Fourier's Number)
 τ = torque (ft lb_r/min.)
 ψ = domain
 ω = angular velocity (rpm)
 ω = relaxation parameter

Superscripts

n = time level

Subscripts

a = annulus
 BH = bottom hole
 c = casing
 ce = cement
 D = dissociated (thawed) zone
 DH = dissociated hydrate zone
 Dp = thawed permafrost zone
 e = extent of reservoir (formation)
 for = formation

fH = hydrate dissociation front
 fp = permafrost thaw front
 H = hydrate
 i = radial grid index
 in = initial
 j = vertical grid index
 jmax = bottom-most grid
 k = index of iteration
 k = region indication (i.e. casing, cement, thawed permafrost, unthawed permafrost, formation, dissociated hydrate, undissociated hydrate)
 l = discrete index of v direction
 m = discrete index of v direction
 meq = equivalent annulus mud
 mi = mud in
 ms = mean annual surface
 o/u = overburden or underburden zone
 p = number of points where the moving boundary intersects the grid lines in the radial direction
 p = permafrost
 pi = inside drill pipe
 pfb = permafrost base
 po = outside drill pipe
 q = number of points where the moving boundary intersects the grid lines in the vertical direction
 S = solid region
 SH = solid hydrate
 Sp = unthawed permafrost
 w = drill pipe (collar) wall

wat = water

wb = wellbore

2.7 REFERENCES

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2.8 APPENDIX A

A. Determination of Convective Heat Transfer Coefficient

For laminar flow of any type of fluid, i.e. Newtonian, Bingham Plastic, or Power Law, the Newtonian value of 4.12 for the Nusselt is number used:

$$\text{Laminar: } N_{Nu} = 4.12 \quad (1A)$$

For turbulent flow of Newtonian fluids or Bingham Plastics, the Seider-Tate equation is used with the following term $(\mu/\mu_w)^{0.14}$ set equal to 1 (Incropera and Dewitt, 1981). For Bingham Plastics, the plastic viscosity is used to calculate the Reynold's and Prandtl numbers.

$$\text{Turbulent: } N_{Nu} = 0.027 N_{Re}^{0.8} Pr^{0.333} \quad (2A)$$

Marshall and Bentsen (1982) recommend the use of a correlation developed by Lakshminarayanan et al (1976) for power-law fluids in turbulent flow:

$$St = 0.0107 N_{Re}^{-0.33} Pr^{-0.67} \quad (3A)$$

In annular flow, the hydraulic diameter of the annulus should be used in these correlations, and the equivalent fluid properties accounting for the drill cuttings and fluid influx into the wellbore should also be used.

B. Determination of Energy Source Terms

The source of heat generation within the wellbore system is a result of the rotational energy due to the work required to rotate the drill string, viscous energy due to frictional losses within the drill pipe, drill bit and annulus, and the work done by the bit.

The thermal energy generated due to rotation and work by the drill bit is calculated by assuming that all of the mechanical energy input by the rotating drive is converted to thermal energy. This energy is then divided 60% to the drill pipe and 40% to the drill bit. The rotational energy input may be calculated by Equation (4A):

$$E_{\text{rot}} = 0.4844 \quad \omega \tau \quad (4A)$$

The total thermal energy generated due to frictional pressure losses in the system may be calculated as

$$E_{\text{fr}} = 1.4843 \Delta P_{\text{fr}} q_m \quad (5A)$$

This energy is then divided among the drill string, drill bit and annulus by the ratios of their respective frictional pressure losses.

3.0 DEVELOPMENT OF GUIDELINES FOR DRILLING IN THE PRESENCE OF HYDRATES

Prior to establishing guidelines for drilling through hydrate containing formations, a parametric study of the reservoir property and drilling parameter effects on hydrate dissociation is required. In addition, potential hydrate precautions can be taken to avoid the problems associated with drilling through those zones.

3.1 Hydrate Stability Zones

With the knowledge of geothermal gradients, pressure - depth - temperature diagrams can be constructed to identify the depths at which gas hydrates may be present. Several thermodynamic studies on the measurement of pressure-temperature relationships for different gas hydrates have been reported in the literature (Deaton and Frost, 1946; Kobayashi and Katz, 1955; Holder, 1976; Wu et al, 1976; Kamath, 1982; Holder and Hand, 1983) and serve as the basis for determination of hydrate stability. Kamath et al (1987) have studied the effects of various parameters on hydrate stability in regions of permafrost. The knowledge of mean annual ground temperature, geothermal gradient, pressure gradient and gas composition is required to fully evaluate potential zones of hydrate occurrence. Other factors influencing hydrate stability include salinity of pore fluids, pore pressure conditions and soil particle effects. Godbole et al (1987) extended the work of Kamath et al (1987) to develop a nomogram (Figure 1) to determine the depths of potential hydrate zones for the wide range of conditions that exist on the North Slope of Alaska and can

be expected to occur in other arctic regions.

Using data from McCleod and Campbell (1961) for sea temperatures, Roadifer et al (1987) extended the work of Godbole et al (1987) and Kamath et al (1987) to develop two additional diagrams (Figure 2 & 3) for determining depths of potential hydrate stability zones in both arctic subsea and subtropic subsea locations. The only requirements for using these diagrams are the sea depth and an estimation of the geothermal gradient below the sea floor. The two main assumptions made in developing diagrams are: the pressure gradient is hydrostatic; and, the hydrates are composed of water and methane only.

3.2. Reservoir Parametric Study

Using a two-dimensional (r-z) cylindrical coordinate thermal hydrate dissociation simulator, Roadifer et al (1987) performed a parametric study of the effects of various reservoir and wellbore parameters on hydrate dissociation rates in arctic regions underlain by permafrost. Parameters studied included: mean annual surface temperature; depth to permafrost base; geothermal gradient within permafrost; geothermal gradient below permafrost; hydrate zone depth; hydrate zone thickness; reservoir porosity; wellbore radius; bottomhole temperature; and equivalent circulating mud density effects on gas influx.

Figure 2: Zone of Hydrate Stability in the Arctic Subsea Region

Figure 3: Zone of Hydrate Stability in the Subtropic Subsea Region

3.2.1 Geothermal Conditions

While important for establishing potential hydrate stability zones, the geothermal parameters, i.e., mean annual surface temperature, depth to permafrost base, and geothermal gradients within and below the permafrost, were found to have negligible effects on the hydrate dissociation rate. This was seen to indicate that heat transfer occurs predominately in the dissociated hydrate zone with the sensible heat required to raise the solid hydrates to dissociation temperature being negligible.

3.2.2. Hydrate Zone Depth

The effect of the hydrate zone depth on the rate of hydrate dissociation is illustrated in Figure 4. The non-linearity of the relationship is explained by the non-linear effect of pressure on the hydrate dissociation temperature, i.e., a hydrostatic pressure gradient was assumed and the hydrate dissociation temperature varies inversely to a logarithmic function of pressure. Because the hydrate dissociation temperature increases with an increase in pressure (depth), the rate of heat transfer, and therefore, hydrate dissociation rate decreases for a fixed wellbore temperature.

3.2.3 Hydrate Zone Thickness

Hydrate zone thickness shows negligible effect on the rate of hydrate dissociation probably due to negligible heat transfer from the overburden and underburden for the thickness range considered. The total hydrates dissociated, however, and

Figure 4 : Effect of Depth of Hydrate on Dissociation Rate

therefore, the surface gas realized are affected directly by the hydrate zone thickness as indicated in Figure 5.

3.2.4 Porosity

The relationship between porosity and hydrate dissociation rate as indicated by the surface gas rate is shown in Figure 6. While significant, this relationship is slightly exaggerated due to the expanded y-axis scale. The maximum difference in hydrate dissociation rates is about 22 percent between the lowest rate at 45 percent porosity and the high at 20 percent porosity.

The increase in the hydrate dissociation rate with a decrease in porosity (down to approximately 20 percent) is due to an increase in the thermal conductivity of the dissociated zone which, because of the fixed wellbore temperature, results in an increase in the heat transfer rate from the wellbore into the dissociated zone.

At the same time, however, the sensible heat required to heat the reservoir rock also increases, but at a different rate. The maximum dissociation rate occurs when for a given reduction in porosity the increase in the heat transfer rate just equals the additional sensible heat required to heat the reservoir rock. For porosities lower than this maximum the additional heat required to heat the reservoir rock is greater than the additional heat supplied to the system.

3.2.5 Drilling Parameter Analysis

The rate of hydrate dissociation depends strongly on the

Figure 5: Effect of Hydrate Zone Thickness on Gas Influx Rate

Figure 6: Relationship Between Porosity and Dissociation Rate

wellbore temperature and the pressure exerted at the hydrate -- dissociated zone interface (both the dissociation temperature and latent heat of dissociation are functions of pressure). The relationship between these two variables and the hydrate dissociation rate (as shown by the surface gas rate) is shown in Figure 7. It should be noted that in addition to affecting the hydrate dissociation rate, the wellbore pressure also affects the gas influx rate from the formation into the wellbore. The pressure effects noted in Figure 7 include both the dissociation rate effect and the gas influx effect.

The effect of pressure on the gas influx rate can be implied from Figure 8 which includes only this effect for various mud densities. This figure indicates that the pressure effect on the gas influx rate is minimal, causing only a minor reduction in the gas influx rate with increased mud density and, therefore, pressure.

3.2.6 Wellbore Radius

In addition to the wellbore temperature and pressure, the wellbore radius also affects the hydrate dissociation rate as indicated by Figure 9. The effect of the wellbore radius on the hydrate dissociation rate is due to an increase in the heat transfer rate with an increase in the wellbore radius. While variations in this parameter are usually not at the discretion of the drilling engineer, the wellbore radius does have a significant effect on the hydrate dissociation rate.

Figure 7: Effect of Temperature and Pressure on the Hydrate Dissociate Rate

Figure 8: Effect of Mud Density on Gas Influx Rate

Figure 9: Effect of Wellbore Radius on Dissociate Rate

3.2.7 Pressure

The drilling and mud engineers have control over three variables which affect the pressure exerted against the formation in the wellbore. These variables are the mud density, viscosity, and circulation rate. The absolute benefits and disadvantages (eg., economics, cutting, removal, etc.) of varying each of these parameters are beyond the scope of this study, but they are covered adequately in most any drilling or mud engineering text. We only concern ourselves here with the relative effects each of these parameters has on the wellbore pressure.

Increase in any one of these parameters will increase the wellbore pressure. Increasing mud weight has the direct effect of increasing the hydrostatic pressure and though less obvious, the frictional pressure drop. The circulation rate and mud viscosity only affect the frictional pressure drop.

Figure 10 shows the relative effects of mud density and circulation rate on the bottomhole pressure. The figure indicates that a drastic increase in the circulation rate is required to achieve the same pressure as the one attained by small increases in mud weight.

There is an additional advantage, however, to increasing the circulation rate. When the hydrates dissociate into gas and water, some of the gas will enter the wellbore, thus reducing the hydrostatic pressure of the mud column. The amount of gas existing in the mud column will be reduced and, therefore, the hydrostatic pressure maximized if the gas entering the wellbore is circulated out as fast as possible. A quantitative analysis

Figure 10: Effect of Mud Density and Circulation Rate on the Bottomhole

of this phenomenon has not been performed at this time.

Figure 11 compares the effects of increasing the mud viscosity and the mud density. Noted here is that large variations in viscosity are required to achieve the same wellbore pressure as moderate increases in the mud weight.

3.2.8 Temperature

The wellbore annulus temperature profile is a function of many variables. As with the wellbore pressure, we concern ourselves here only with those parameters that may be controlled directly by the drilling or mud engineers. A discussion of other variables is available in the literature (Edwardson et al, 1962; Tragesser et al, 1967; Holmes and Swift, 1970; Keller et al, 1973; Marshall and Bentsen, 1982; Corre et al, 1984; and Thompson, 1985).

The primary parameters of concern are the mud inlet temperature, density, circulation rate, and whether or not the hole has been cased. Figure 12 shows a comparison of the bottomhole temperatures generated due to inlet mud temperature for an uncased well and a well cased to the permafrost base. Two noteworthy effects are seen in this plot. First, the change in the bottomhole temperature is much less than the change in the mud inlet temperature. Second, casing the permafrost zone results in significantly higher bottomhole temperatures.

The ramifications of these results depend on the particular method of hydrate control being used, i.e., limiting or promoting

Figure 11: Effect of Mud Density and Viscosity on the Bottomhole Pressure

Figure 12: Effect of Casing and Mud Inlet Temperature on the Bottomhole Temperature

hydrate dissociation. If the goal is to limit hydrate dissociation, casing should not be run until the potential hydrate bearing depths have been drilled, assuming this will not cause significant new problems in the permafrost region. In subsea locations, the corollary to this is not to use a riser casing so the cooling effect of the sea can be taken advantage of. If the goal is to promote hydrate dissociation while drilling, the current practice of casing off the permafrost zone as soon as it has been penetrated should be followed.

The effect of mud density and circulation rate on bottomhole temperature is a much more complex problem as indicated by Figure 13. To understand the implications of this figure, a discussion of the heat transfer mechanisms present in the wellbore is required.

Within the wellbore, heat transfer occurs due to vertical convection down the drill string and up the annulus, radial convection between fluid, pipe wall and formation, and lastly due to heat generation. When the mud circulation is increased, vertical convection increases, tending to increase the bottomhole temperature; because the boundary layer convection coefficient increases, radial heat convection increases, tending to decrease the bottomhole temperature; lastly, the frictional pressure drop increases, resulting in higher heat generation and an increase in temperature.

An example will help to clarify these mechanisms. Consider the case of the 14 lb/gal mud in Figure 13. At a circulation rate of 100 gal/min, the flow regime is laminar in both the drill

Figure 13: Effect of Mud Density and Circulation Rate on the Bottomhole Temperature

string and the annulus. When the flow rate is increased to 200 gal/min, the flow inside the drill string becomes turbulent, and the convective heat transfer coefficient increases from 8.4 to 146 (Btu/ft²-hr-F). The flow in the annulus, however, has remained laminar with no change in the convective heat transfer coefficient. The heat transfer, therefore, has remained constant between the formation and the annular fluid, whereas heat transfer has increased markedly between the cooler annular fluid and warmer drill string fluid, resulting in the observed temperature drop.

Increasing the flow rate to 300 gal/min results in an additional increase in the drill string convection coefficient (to 200 Btu/ft²-hr-F, a 38% increase), but is counteracted by a 38 percent increase in the heat generation or source term (from 40.3 to 55.6 Btu/ft-hr) and an increase in the vertical convection. This results in a slight increase in the bottomhole temperature. As the flow rate is increased to 400 gal/min, the bottomhole temperature is dramatically reduced. The reason for this sharp drop is quite simple; the flow regime in the annulus has become turbulent, resulting in an increase in the wellbore convective heat transfer coefficient from 28 to 348 (Btu/ft²-hr-F) and a corresponding increase in the heat losses to the formation. As the flow rate is again increased, the effects of vertical convection and heat generation once again become significant.

The above discussion provides guidelines for selection of a flow regime for the drilling fluid. If the goal is to prevent hydrate dissociation, the drilling fluid should be in the

turbulent flow regime in the annulus. If the goal is to promote hydrate dissociation, a laminar flow regime is desired in the annulus.

3.3. Selection of Parameters

The relative effects of many drilling and mud parameters on the wellbore pressures and temperatures (and therefore hydrate dissociation rate and gas influx rate) have been shown and discussed. The precise combination of these parameters to be used to achieve the desired results cannot be stated as each new well is unique and controlled by many factors, e.g., economics, legal restrictions, equipment availability, etc. What can be stated, however, is the temperature and pressure necessary to keep hydrate dissociation within the limits of the drilling equipment, or vice versa, design criteria for the surface degassing equipment can be established for the maximum temperatures and minimum pressures expected to occur over the hydrate zone. These results are presented in nomogram form in Figure 14-16, which represent three different uses of the nomogram. Example uses of the nomogram are presented in the appendix.

EXAMPLE #1

$P = 1750$ (psia)
 $T_m = 96$ (°F)
 $D_{wb} = 8.375$ (in)
 $H_{hyd} = 50$ (ft)

$Q_g = 28$ (SCFM)

Figure 14: Nomogram for Estimation of Parameters for Drilling Through Hydrates

Figure 15: Nomogram for Estimation of Parameters for Drilling Through Hydrates

EXAMPLE #2		
$Q_g = 80$	(SCFM)	
$T_m = 100$	(°F)	
$D_{wb} = 11$	(in)	
$H_{Hyd} = 100$	(ft)	
<hr/>		
$P = 1420$	(psia)

EXAMPLE #3

$P = 1000$ (psia)
 $Q_g = 50$ (SCFM)
 $D_{wb} = 10$ (in)
 $H_{hyd} = 75$ (ft)
 $T_m = 90$ (°F)

Figure 16: Nomogram for Estimation of Parameters for Drilling Through Hydrates

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SECTION IV:

**EXPERIMENTAL STUDY OF UNCONSOLIDATED
GAS HYDRATE CORES**

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EXPERIMENTAL STUDY OF UNCONSOLIDATED GAS HYDRATE CORES

1. Objective:

The experimental research on unconsolidated gas hydrate cores has the following major goals:

- a. Development of experimental techniques to form gas hydrates in the unconsolidated sand cores.
- b. Measurement of permeability of gas through these unconsolidated gas hydrate cores as a function of hydrate saturation.
- c. Study of hydrate formation mechanism.
- d. Study of dissociation of the hydrate cores under various conditions such as depressurization, hot brine and steam injection and measurement of gas production rates.
- e. Study of hydrate dissociation mechanism under above conditions to determine conduction and convection heat transfer and mass transfer phenomena.

2. Perspective:

So far, very few studies have been done on hydrate formation and dissociation in porous media, and no experimental data is available on gas production rates during injection of hot brine, steam, or depressurization methods to dissociate hydrates in the porous media. A better understanding of heat and mass transfer effects would be helpful in modelling hydrate production methods so that some of these techniques can be developed commercially. Data gathered in this study will be helpful in evaluating these production methods.

3. Work Performed During The First Year

Although this task had no deliverables for the first year and, according to the work plan provided in the proposal, experimental work was proposed to begin in the

second year, we did start experimental work which is reported in this section.

During the first quarter of the first year, we completed the design of our experimental set up and ordered the equipment components. During the second quarter, we began receiving the equipment components. Late in the second and third quarters we completed the assembly of all the equipment components and necessary piping and fittings. After completion of the experimental set up, we completed preliminary testing of various components, calibration of flow meters, wet test meters, pumps, pressure and temperature measurement devices, and measurement of volumetrics of various components.

In the last quarter, we began the experimental work. Initially, we tested several methods of forming hydrate cores to suit our experimental needs. Then we conducted several runs to measure permeability of gas through hydrate cores as a function of hydrate saturation. Currently, we are in the process of gathering more experimental data on hydrate permeability measurements. The next section provides the experimental set up description, experimental methods employed, and problems encountered during data gathering.

4. Experimental Set-up

Figure 1 shows the schematic diagram of the experimental apparatus for hydrate core formation and dissociation experiments and permeability measurements. Table 1 provides a list of the equipment.

The hydrate core holder is a specially designed unit manufactured by Setra, Inc. The core holder has an internal diameter of 4 inches and a length of 12 inches. It has two flanges on the top and bottom. The core holder has a methanol jacket through which cold methanol is circulated continuously to maintain the core holder at a desired temperature. On one side of the core holder are three pressure taps at 3, 6, and 9 inch distances from the bottom. Pressure transducers

1. Temperature Controller
2. Methanol Bath
3. Refrigeration Coils
4. Heater
5. Digital Temp Indicator
6. Core Holder
- 7,8,9. Pressure Transducers
10. To Methanol Bath
11. Pressure Indicator
12. Gas Flow Meter
13. Gas Cylinder
14. Wet Test Flow Meter
15. Water Tank
16. Gas Water Separator
17. To Vacuum Pump
18. Pressure Gauge
19. Back Pressure Regulator
20. Moist Trap
21. Temperature Control
22. Gas Flow Meter
23. Gas Flow Control
24. Gas Compressor
25. Water Flow Meter
26. Water Pump

Figure 1: Schematic Diagram of Experimental Setup for Hydrate Core Experiment.

TABLE 1**List of Equipment for Experimental Study of Hydrate Cores**

<u>Quantity</u>	<u>Model No</u>	<u>Equipment Received</u>	<u>Company</u>
2	3270	Mass Flow Meter	Cole-Parmer
1	BA-3275-00	Flow Controller	Cole-Parmer
1	—	Sample Cylinder	D.B. Robinson
3	PK-301-2KGV	Pressure Transducers	OMEGA Eng.
1	PRC-3500-P#	Pressure Monitor	OMEGA Eng.
1	BP-1-V	Back Pressure Regulator	TEMCO
1	RTE-4	Bench Top Refrigerated Bath Circulator	Neslab
3	CM	Heise Pressure Gauges	Heise
1	63115	Wet Test Gas Meter	Precision Sc.
1	17-T-40	Water Gas Sample	Jerguson
1	—	Core Holder	Centra
1	3G	Const Metric Pump	LDC Milton Roy
1	AGD-15	Gas Compressor	Haskel
1	1397	Vacuum Pump	Welch
1	AC-523	Air Compressor	National Air
1	651	Resistance Thermometer	OMEGA Eng.
1	DV-6	Vacuum Pump Gauge	Hasting
1	205-002	Flow Meter/Water	Headland

are hooked up at these three pressure ports to monitor pressure drops within the core during permeability experiments. On the opposite side, there are three thermocouple ports through which thermocouples are inserted to measure temperature profiles within the core. The top flange of the core holder has three ports for gas outlet, water inlet and temperature sensor. The bottom flange has one port for gas inlet. With anticipation of plugging of core due to hydrate formation causing no gas flow and increase in inlet pressure, we decided to use a specially designed system for gas inlet. This specially designed gas inlet system consisted of three gas spargers located at three different positions within the core and hooked up to gas inlets through three concentric tubes. This system allowed inlet of gas at three different locations of the core so that if the bottom sparger plugs up due to hydrate formation the top one can allow gas flow. This gas inlet assembly was discontinued in the later experiments due to change in experimental procedures.

Bench top refrigerated bath circulator (Model RTE-4) manufactured by Neslab, Inc., is used for cooling methanol, controlling the temperature of methanol and circulating it through the jacket of the hydrate core holder at desired temperatures. Three pressure transducers (Model #PK-301-2KGV) are hooked to core holder ports at the side and connected to digital pressure monitor (Model #PRC-3500-P3), all manufactured by Omega Engineering, and have a range of 0-2000 psia pressure. All three platinum resistance thermometers are inserted at three temperature ports of the core holder and connected to digital temperature indicator ($\pm 0.1^{\circ}\text{C}$ divisions).

The gas inlet line has a gas flow meter (0-1000 cc/min, Model #3270, Cole Parmer) and a gas flow controller (0-100% range, Model # BA-3275-00, Cole Parmer, 0.1% flow accuracy). The inlet gas line was passed through a series of coils inserted in the methanol bath for precooling of inlet gas prior to core holder.

The gas outlet line also has a gas flow meter to measure the outlet gas flow during permeability measurements. (In addition, a wet test flow meter was also hooked up to the gas outlet line.)

To achieve continuous gas flow in the core holder without loss of significant amounts of gas, a gas compressor was connected to the gas outlet line. This is a air driven gas compressor (Haskel Model #AGD-15) and is driven by an air compressor (100 psi air supply pressure). The compressed outlet gas is recycled back to the core holder. This compressor and recycling procedure was discontinued in the later experiments due to severe pressure and gas flow fluctuations in the inlet line. Also installed in the inlet and outlet line for gas are the Heise pressure gauges (Model M, 0-2000 psig).

The water inlet line of the core holder is hooked to a constant rate high pressure water pump (0-1.6 lit/min capacity, LDC Milton Roy Co.). This pump is used for injecting hot brine or water in the hydrate core holder during dissociation experiments. The hot water or brine supply to the pump comes from a high pressure vessel termed as hot water or brine tank. In this vessel the brine is heated to a temperature by an immersion heater controlled by a temperature controller such that the sensor inserted into the liquid phase of the core holder senses a constant desired temperature. To determine material balance on gas produced during hydrate dissociation and water injected, a liquid level of the brine (or water) in the tank is measured by a liquid level indicator (Jerguson Gauge). This also acts as a gas water separator for a line that allows the flow of dissociated gas and water from the core holder and is connected to a back pressure regulator and wet test meter to measure gas production rates during dissociation experiments. All system parts could be evacuated independently by a vacuum pump.

The thermocouples, pressure transducers, water pump, methanol bath, wet test meter, gas flow meter, and gas flow controllers were calibrated prior to the

start of the experiments.

5. Experimental Techniques

a. Hydrate Formation:

We tried several methods and variations of hydrate formation. These methods are summarized as follows:

Method 1:

In this method we used a gas sparger system within the core. Initially, 20 mesh Ottawa sand was charged by the core holder and then packed using a vibrator assembly. The porosity was determined and then the core was saturated completely with water. After closing the core holder and evacuating it for 15-20 minutes, the temperature of the core holder was dropped and held at a constant value of 2 to 3°C. Methane at an inlet pressure of 1,000 psi (6.7 MPD) and flow rate of 50-60 cc/min was continuously supplied from the bottom of the core holder. The compressor assembly was also used in this method to recycle the outlet methane gas back to the core holder. In this method we did succeed in the formation of hydrates in the pores of the core and, we also observed in one experiment, plugging of the sparger opening due to hydrate formation. In this case we changed the gas supply to the next sparger to continue the flow. Several problems encountered led us to discontinue this method. One problem was that due to the upward flow of gas, the water from the core was displaced by the gas and large amounts of hydrates also formed on the top (outside of the core) which was undesirable for the experimental measurements. Other problems were that the sparger assembly caused problems of cleaning the core and charging sand and compaction.

Another variation of this method was to remove gas sparger assembly

and injecting gas from the top instead of the bottom. However, this method also was discontinued due to entrainment of water in the lines and in the flow meter which resulted in erroneous gas flow measurements.

Due to problems of water entrainment in the lines, we decided to switch to another variation of this method. In this variation, we installed semipermeable plates on the gas outlet line so that no water can flow through the lines but allow gas to flow through. Although this method was partially successful in not allowing water beyond semi-permeable plates, the problems of material balance were encountered due to large amounts of water that were displaced from the core holder and remained in line between core holder and semipermeable plate. Thus, this method can be successfully used by placing the semipermeable plate within the core holder itself. This will provide all of the water in the core to remain within the core. This variation will be tried later during the next quarter.

Method 2:

In this method, we used finely divided crystal of ice (frost, approximately 400 micron size) instead of saturating the core with water. The sand and frost were thoroughly mixed and compacted. This is the same method as discussed by Kamath (1984). Prior to charging sand and frost, the core holder was cooled to -15°C so that no melting of the frost would take place during charging. It is very essential to maintain the quality of frost to be high (i.e. no wet frost). This method was very successful in terms of hydrate formation rates. Again we tried several variations of this method so that we could make reliable measurements of permeability of the core.

One variation, was to continuously inject gas at a desired rate. This method was discontinued due to problems of pressure and flow fluctuations from the compressor. Instead of recycling the gas we tried a continuous fresh

supply of gas so that pressure and flow fluctuations could be eliminated. This procedure required a large consumption of gas and also posed problems of material balance. We also varied the direction of the gas injection. Instead of upward gas flow we used downward gas flow.

The most economical, as well as successful method, was forming hydrates in batch gas injection process. The procedure was exactly the same as described by Kamath (1984). The only modifications were permeability measurements as described later.

b. Permeability Measurements:

In order to measure permeability of gas through the hydrate core we implemented the following method:

After charging frost and sand, compacting the core and evacuation, the core holder pressure was raised to 600 psia and at constant temperature of 0.5°C. The initial gas permeability when no hydrates are formed was measured by continuously flowing gas from the top at a rate of 400-500 cc/min for 15 minutes. During these 15 minutes of gas flow, at every minute, the gas flow rate and pressure drops were measured. From these readings, initial core permeability was determined using Darcy's law. Precautions were taken to make sure the gas flows were within the range for which Darcy's law is valid. After that, the gas flow was stopped and systems pressure was raised to 700 psia. Hydrates were allowed to form as observed by pressure within the core dropping with time. When pressure dropped to 600 psia, the amount of conversion of frost to hydrates was determined.

6. Preliminary Results

We observed significant increases in pressure drops and decreases in permeability due to hydrate formation. Typically, starting with 700 MD

initial core permeability at 70% hydrate saturation the permeability dropped to 3-4 MD.

Tables 2 and 6 give the experimental conditions of our experiments. Figure 2 shows various runs for which hydrate conversion (or saturation) versus time is plotted. Figure 3 shows permeability of the core versus hydrate saturation.

Note that, although the initial permeability varies from run to run depending upon the properties of the core, the ratio of core permeability at any hydrate saturation to initial permeability can be correlated as a function of hydrate saturation.

Currently, we are in the process of collecting more data and obtaining more reliable, reproducibility of the data.

CONVERSION VS TIME FOR RUNS 1 THROUGH 5

Figure 2: Hydrate Saturation (Conversion) in the Core Versus Time for Various Runs

CORE PERMEABILITY VS PERCENT HYDRATES

Figure 3: Gas Permeability in the Core as a Function of Hydrate Saturation in the Core

RESULTS OF METHANE HYDRATE FORMATION RUNS

METHANE HYDRATE FORMATION RUN # 1

DATE RUN STARTED:10-19-1987

DATE RUN ENDED:10-22-1987

GRAMS OF H2O- 819.400

GRAMS OF SAND- 831.800

HEIGHT OF THE CORE- 22.35CM.

ROOM TEMPERATURE- 21.0000DEG.C

TEMP.OF GAS LEAVING WET TEST METER- 16.7000DEG.C

BAROMETRIC PRESSURE- 742.800MM.HG

VAP.PRESSURE OF WATER AT TWIM- 14.100MM.HG

ICE TO SAND VOL.RATIO- 2.782

ICE TO SAND MASS RATIO- 0.985

PERCENTAGE VOIDS IN THE CORE- 32.962

GMOL.METHANE FOR 100 PERCENT CONVERSION- 7.909881

HYDRATE FORMATION RUN INPUT DATA

TIME (HR)	P1 (PSIA)	P3 (PSIA)	PL (PSIA)	PM (PSIA)	PR (PSIA)	T1RTD (DEG.C)	T2RTD (DEG.C)	FIREAD	WVTH (LIT)
0.00	593.00	594.00	595.00	593.00	594.00	-0.20	-0.80	0.00	0.00
0.17	586.00	584.00	587.00	585.00	586.00	-0.20	-0.80	0.00	0.00
0.18	586.00	584.00	587.00	585.00	586.00	-0.20	-0.80	18.60	0.33
0.20	582.00	582.00	584.00	582.00	583.00	-0.20	-0.80	17.30	0.66
0.22	580.00	578.00	581.00	579.00	581.00	-0.20	-0.80	16.70	0.98
0.27	575.00	572.00	576.00	574.00	575.00	-0.40	-1.10	36.70	2.30
0.30	573.00	568.00	574.00	572.00	573.00	-0.40	-1.10	36.50	2.79
0.33	572.00	566.00	572.00	570.00	571.00	-0.40	-1.10	36.50	3.42
0.42	794.00	792.00	796.00	793.00	795.00	-0.30	-0.80	0.00	3.42
0.75	767.00	764.00	770.00	766.00	768.00	-0.30	-0.80	0.00	0.00
0.92	756.00	751.00	760.00	757.00	759.00	-0.30	-0.80	0.00	0.00
1.42	718.00	709.00	721.00	717.00	719.00	0.30	-0.90	0.00	0.00
2.83	612.00	614.00	645.00	655.00	616.00	0.40	-1.00	0.00	0.00
3.42	586.00	586.00	645.00	654.00	583.00	0.40	-1.00	0.00	8.15
4.00	554.00	556.00	642.00	650.00	653.00	0.40	-1.00	17.10	9.20
4.03	554.00	556.00	642.00	650.00	653.00	0.40	-1.00	17.50	11.30
4.10	530.00	530.00	642.00	612.00	632.00	0.40	-1.00	17.50	12.40
4.13	524.00	524.00	642.00	592.00	631.00	0.30	-0.90	0.00	14.30
4.33	610.00	585.00	642.00	576.00	644.00	0.30	-0.90	0.00	0.00
4.42	783.00	783.00	783.00	783.00	783.00	0.30	-0.90	0.00	0.00
4.92	746.00	746.00	744.00	614.00	741.00	-0.10	0.40	0.00	0.00
12.58	398.00	400.00	401.00	460.00	399.00	0.50	0.00	0.00	14.10
15.42	401.00	402.00	404.00	461.00	400.00	4.50	4.40	0.00	31.60
15.50	602.00	603.00	603.00	462.00	600.00	3.00	3.80	36.00	31.60
15.92	570.00	572.00	502.00	449.00	569.00	3.20	3.70	36.00	32.25
15.95	566.00	568.00	497.00	447.00	564.00	2.80	3.20	36.00	32.80
15.98	564.00	565.00	495.00	446.00	562.00	3.00	3.60	36.00	33.03
16.02	563.00	564.00	494.00	445.00	560.00	4.40	9.10	0.00	33.40
16.33	975.00	975.00	570.00	459.00	906.00	2.70	2.50	0.00	0.00
19.42	986.00	986.00	919.00	533.00	796.00	0.70	1.20	0.00	0.00
19.17	968.00	968.00	817.00	483.00	765.00	-0.40	0.40	0.00	36.81
19.45	602.00	602.00	603.00	456.00	580.00	-0.70	-0.10	34.50	38.65
19.58	596.00	596.00	598.00	450.00	556.00	-0.20	0.10	31.00	39.65
19.61	594.00	593.00	595.00	448.00	546.00	-0.60	-0.20	27.00	40.60
19.65	591.00	591.00	593.00	446.00	541.00	-0.40	0.10	41.00	41.50
19.69	588.00	589.00	590.00	445.00	535.00	0.10	-0.20	0.00	0.00
19.92	702.00	702.00	703.00	440.00	532.00	-0.20	-0.40	0.00	0.00
21.42	681.00	682.00	683.00	509.00	533.00	-0.40	-0.70	0.00	0.00
22.58	670.00	671.00	675.00	509.00	558.00	0.00	-0.20	0.00	0.00
23.33	663.00	664.00	667.00	509.00	556.00	1.10	-0.30	0.00	9.50
23.42	600.00	600.00	603.00	509.00	555.00	-0.90	-0.80	29.70	10.50
23.50	591.00	592.00	594.00	509.00	554.00	-0.30	-0.40	38.90	11.22
23.53	589.00	590.00	593.00	509.00	554.00	-0.50	-0.60	35.10	11.32
23.57	590.00	592.00	593.00	509.00	553.00	-0.20	-0.30	34.00	12.22
23.60	592.00	594.00	597.00	509.00	551.00	-0.50	-0.60	33.00	12.42
23.63	595.00	596.00	600.00	509.00	550.00	-0.60	0.30	0.00	0.00
23.67	766.00	768.00	771.00	509.00	550.00	-0.20	-0.30	0.00	0.00
24.67	754.00	755.00	758.00	508.00	548.00	0.40	0.10	0.00	0.00
25.92	747.00	748.00	752.00	508.00	543.00	0.00	-0.30	0.00	0.00
27.42	740.00	741.00	743.00	507.00	519.00	-0.10	-0.40	0.00	0.00
29.17	734.00	734.00	737.00	507.00	504.00	-0.20	-0.60	0.00	0.00
39.92	707.00	708.00	711.00	505.00	472.00	-0.20	-0.60	0.00	0.00
45.42	698.00	700.00	701.00	505.00	499.00	-0.20	-0.60	0.00	0.00
45.83	740.00	740.00	742.00	505.00	503.00	-0.60	-0.70	0.00	19.18
46.33	599.00	600.00	603.00	505.00	514.00	-0.30	-0.40	16.50	21.70
46.55	585.00	586.00	588.00	505.00	505.00	-0.40	-0.70	15.60	22.16
46.58	584.00	585.00	587.00	505.00	504.00	-0.40	-0.70	16.60	22.75
46.62	582.00	584.00	586.00	505.00	504.00	0.00	0.30	0.00	22.79

RESULTS OF HYDRATE RUN

TIME (HR)	PRAR (PSIA)	TRAR (DEG.C)	QBAR (CC/MIN)	CONV (%)	TIME	CHDLO	CHDOLG	CHDOLN	CHDOLP	CHDOLV
0.000	593.500	0.000	0.000	0.000	0.0000	1.5200	1.5200	0.0000	0.0000	0.0000
0.167	585.000	0.000	0.000	0.655	0.1670	1.5200	1.5200	0.0000	0.0000	0.0000
0.183	585.000	0.000	207.593	0.772	0.1830	1.5200	1.5200	0.0000	0.0000	0.0000
0.200	582.000	0.000	198.532	1.100	0.2000	1.5200	1.5200	0.0000	0.0000	0.0000
0.217	579.000	0.000	191.988	1.423	0.2170	1.5200	1.5200	0.0000	0.0000	0.0000
0.267	573.500	-0.250	567.605	1.680	0.2670	1.5200	1.5200	0.0000	0.0000	0.0000
0.300	570.500	-0.250	370.151	2.225	0.3000	1.5200	1.5200	0.0000	0.0000	0.0000
0.333	569.000	-0.250	403.221	2.579	0.3330	1.5200	1.5200	0.0000	0.0000	0.0000
0.417	793.000	-0.250	0.000	2.579	0.4170	1.5200	1.5200	0.0000	0.0000	0.0000
0.750	765.500	-0.050	0.000	4.744	0.7500	1.5200	1.5200	0.0000	0.0000	0.0000
0.917	753.500	-0.050	0.000	5.670	0.9170	1.5200	1.5200	0.0000	0.0000	0.0000
1.417	713.500	-0.050	0.000	8.755	1.4170	1.5200	1.5200	0.0000	0.0000	0.0000
2.833	613.000	0.200	0.000	16.549	2.8330	1.5200	1.5200	0.0000	0.0000	0.0000
3.417	586.000	0.200	0.000	18.630	3.4170	1.5200	1.5200	0.0000	0.0000	0.0000
4.000	555.000	0.200	0.000	21.018	4.0000	1.5200	1.5200	0.0000	0.0000	0.0000
4.033	555.000	0.200	367.214	20.728	4.0330	1.5200	1.5200	0.0000	0.0000	0.0000
4.100	530.000	0.200	618.030	21.810	4.1000	1.5200	1.5200	0.0000	0.0000	0.0000
4.133	524.000	0.200	381.813	21.961	4.1330	1.5200	1.5200	0.0000	0.0000	0.0000
4.333	597.500	0.200	0.000	21.961	4.3330	1.5200	1.5200	0.0000	0.0000	0.0000
4.417	783.000	0.200	0.000	21.961	4.4170	1.5200	1.5200	0.0000	0.0000	0.0000
4.917	746.000	0.200	0.000	24.812	4.9170	1.5200	1.5200	0.0000	0.0000	0.0000
12.580	399.000	0.650	0.000	51.600	12.5800	1.5200	1.5200	0.0000	0.0000	0.0000
15.420	401.500	0.750	0.000	51.419	15.4200	1.5200	1.5200	0.0000	0.0000	0.0000
15.500	602.500	4.950	0.000	51.419	15.5000	1.5200	1.5200	0.0000	0.0000	0.0000
15.920	571.000	3.900	0.000	53.641	15.9200	1.5200	1.5200	0.0000	0.0000	0.0000
15.950	567.000	3.950	404.461	54.173	15.9500	1.5200	1.5200	0.0000	0.0000	0.0000
15.980	564.500	3.500	380.939	54.566	15.9800	1.5200	1.5200	0.0000	0.0000	0.0000
16.020	563.500	3.800	305.250	55.132	16.0200	1.5200	1.5200	0.0000	0.0000	0.0000
16.130	975.000	7.250	0.000	55.132	16.1300	1.5200	1.5200	0.0000	0.0000	0.0000
16.420	986.000	3.100	0.000	60.818	16.4200	1.5200	1.5200	0.0000	0.0000	0.0000
19.170	968.000	1.450	0.000	61.793	19.1700	1.5200	1.5200	0.0000	0.0000	0.0000
19.450	602.000	0.500	0.000	62.414	19.4500	1.5200	1.5200	0.0000	0.0000	0.0000
19.590	596.000	0.100	675.103	62.371	19.5900	1.5200	1.5200	0.0000	0.0000	0.0000
19.610	591.500	0.450	452.356	62.577	19.6100	1.5200	1.5200	0.0000	0.0000	0.0000
19.650	591.000	0.100	412.346	62.629	19.6500	1.5200	1.5200	0.0000	0.0000	0.0000
19.660	591.000	0.350	495.365	63.028	19.6600	1.5200	1.5200	0.0000	0.0000	0.0000
19.700	591.000	0.450	0.000	63.028	19.7000	1.5200	1.5200	0.0000	0.0000	0.0000
19.720	591.000	0.100	0.000	64.559	19.7200	1.5200	1.5200	0.0000	0.0000	0.0000
19.740	591.000	0.100	0.000	64.559	19.7400	1.5200	1.5200	0.0000	0.0000	0.0000
19.760	591.000	0.100	0.000	64.559	19.7600	1.5200	1.5200	0.0000	0.0000	0.0000
19.780	591.000	0.100	0.000	64.559	19.7800	1.5200	1.5200	0.0000	0.0000	0.0000
19.800	591.000	0.100	0.000	64.559	19.8000	1.5200	1.5200	0.0000	0.0000	0.0000
19.820	591.000	0.100	0.000	64.559	19.8200	1.5200	1.5200	0.0000	0.0000	0.0000
19.840	591.000	0.100	0.000	64.559	19.8400	1.5200	1.5200	0.0000	0.0000	0.0000
19.860	591.000	0.100	0.000	64.559	19.8600	1.5200	1.5200	0.0000	0.0000	0.0000
19.880	591.000	0.100	0.000	64.559	19.8800	1.5200	1.5200	0.0000	0.0000	0.0000
19.900	591.000	0.100	0.000	64.559	19.9000	1.5200	1.5200	0.0000	0.0000	0.0000
19.920	591.000	0.100	0.000	64.559	19.9200	1.5200	1.5200	0.0000	0.0000	0.0000
19.940	591.000	0.100	0.000	64.559	19.9400	1.5200	1.5200	0.0000	0.0000	0.0000
19.960	591.000	0.100	0.000	64.559	19.9600	1.5200	1.5200	0.0000	0.0000	0.0000
19.980	591.000	0.100	0.000	64.559	19.9800	1.5200	1.5200	0.0000	0.0000	0.0000
20.000	591.000	0.100	0.000	64.559	20.0000	1.5200	1.5200	0.0000	0.0000	0.0000
20.020	591.000	0.100	0.000	64.559	20.0200	1.5200	1.5200	0.0000	0.0000	0.0000
20.040	591.000	0.100	0.000	64.559	20.0400	1.5200	1.5200	0.0000	0.0000	0.0000
20.060	591.000	0.100	0.000	64.559	20.0600	1.5200	1.5200	0.0000	0.0000	0.0000
20.080	591.000	0.100	0.000	64.559	20.0800	1.5200	1.5200	0.0000	0.0000	0.0000
20.100	591.000	0.100	0.000	64.559	20.1000	1.5200	1.5200	0.0000	0.0000	0.0000
20.120	591.000	0.100	0.000	64.559	20.1200	1.5200	1.5200	0.0000	0.0000	0.0000
20.140	591.000	0.100	0.000	64.559	20.1400	1.5200	1.5200	0.0000	0.0000	0.0000
20.160	591.000	0.100	0.000	64.559	20.1600	1.5200	1.5200	0.0000	0.0000	0.0000
20.180	591.000	0.100	0.000	64.559	20.1800	1.5200	1.5200	0.0000	0.0000	0.0000
20.200	591.000	0.100	0.000	64.559	20.2000	1.5200	1.5200	0.0000	0.0000	0.0000
20.220	591.000	0.100	0.000	64.559	20.2200	1.5200	1.5200	0.0000	0.0000	0.0000
20.240	591.000	0.100	0.000	64.559	20.2400	1.5200	1.5200	0.0000	0.0000	0.0000
20.260	591.000	0.100	0.000	64.559	20.2600	1.5200	1.5200	0.0000	0.0000	0.0000
20.280	591.000	0.100	0.000	64.559	20.2800	1.5200	1.5200	0.0000	0.0000	0.0000
20.300	591.000	0.100	0.000	64.559	20.3000	1.5200	1.5200	0.0000	0.0000	0.0000
20.320	591.000	0.100	0.000	64.559	20.3200	1.5200	1.5200	0.0000	0.0000	0.0000
20.340	591.000	0.100	0.000	64.559	20.3400	1.5200	1.5200	0.0000	0.0000	0.0000
20.360	591.000	0.100	0.000	64.559	20.3600	1.5200	1.5200	0.0000	0.0000	0.0000
20.380	591.000	0.100	0.000	64.559	20.3800	1.5200	1.5200	0.0000	0.0000	0.0000
20.400	591.000	0.100	0.000	64.559	20.4000	1.5200	1.5200	0.0000	0.0000	0.0000
20.420	591.000	0.100	0.000	64.559	20.4200	1.5200	1.5200	0.0000	0.0000	0.0000
20.440	591.000	0.100	0.000	64.559	20.4400	1.5200	1.5200	0.0000	0.0000	0.0000
20.460	591.000	0.100	0.000	64.559	20.4600	1.5200	1.5200	0.0000	0.0000	0.0000
20.480	591.000	0.100	0.000	64.559	20.4800	1.5200	1.5200	0.0000	0.0000	0.0000
20.500	591.000	0.100	0.000	64.559	20.5000	1.5200	1.5200	0.0000	0.0000	0.0000
20.520	591.000	0.100	0.000	64.559	20.5200	1.5200	1.5200	0.0000	0.0000	0.0000
20.540	591.000	0.100	0.000	64.559	20.5400	1.5200	1.5200	0.0000	0.0000	0.0000
20.560	591.000	0.100	0.000	64.559	20.5600	1.5200	1.5200	0.0000	0.0000	0.0000
20.580	591.000	0.100	0.000	64.559	20.5800	1.5200	1.5200	0.0000	0.0000	0.0000
20.600	591.000	0.100	0.000	64.559	20.6000	1.5200	1.5200	0.0000	0.0000	0.0000
20.620	591.000	0.100	0.000	64.559	20.6200	1.5200	1.5200	0.0000	0.0000	0.0000
20.640	591.000	0.100	0.000	64.559	20.6400	1.5200	1.5200	0.0000	0.0000	0.0000
20.660	591.000	0.100	0.000	64.559	20.6600	1.5200	1.5200	0.0000	0.0000	0.0000
20.680	591.000	0.100	0.000	64.559	20.6800	1.5200	1.5200	0.0000	0.0000	0.0000
20.700	591.000	0.100	0.000	64.559	20.7000	1.5200	1.5200	0.0000	0.0000	0.0000
20.720	591.000	0.100	0.000	64.559	20.7200	1.5200	1.5200	0.0000	0.0000	0.0000
20.740	591.000	0.100	0.000	64.559	20.7400	1.5200	1.5200	0.0000	0.0000	0.0000
20.760	591.000	0.100	0.000	64.559	20.7600	1.5200	1.5200	0.0000	0.0000	0.0000
20.780	591.000	0.100	0.000	64.559	20.7800	1.5200	1.5200	0.0000	0.0000	0.0000
20.800	591.000	0.100	0.000	64.559	20.8000	1.5200	1.5200	0.0000	0.0000	0.0000
20.820	591.000	0.100	0.000	64.559	20.8200	1.5200	1.5200	0.0000	0.0000	0.0000
20.840	591.000	0.100	0.000	64.559	20.8400	1.5200	1.5200	0.0000	0.0000	0.0000
20.860	591.000	0.100	0.000	64.559	20.8600	1.5200	1.5200	0.0000	0.0000	0.0000
20.880	591.000	0.100	0.000	64.559	20.8800	1.5200	1.5200	0.0000	0.0000	0.0000
20.900	591.000	0.100	0.000	64.559	20.9000	1.5200	1.5200	0.0000	0.0000	0.00

SECTION 4

RESULTS OF NITRATE RUN

TIME (HR)	PMR (PPT)	TRR (DEG.C)	QRR (CC/MIN)	CONV (%)	TIME	QRR	PMR	TRR	QRR	CONV
0.000	593.500	0.000	0.000	0.000	1.1000	1.1000	1.1000	1.1000	1.1000	1.1000
0.167	585.000	0.000	0.000	0.655	0.1670	1.1320	1.1141	1.1000	1.1000	1.1000
0.183	585.000	0.000	207.593	0.772	0.1830	1.1392	1.1141	1.1000	1.1000	1.1000
0.200	582.000	0.000	198.532	1.100	0.2000	1.1368	1.1141	1.1000	1.1000	1.1000
0.217	579.000	0.000	191.828	1.423	0.2170	1.1441	1.1141	1.1000	1.1000	1.1000
0.257	573.500	-0.250	567.605	1.680	0.2570	1.1341	1.1141	1.1000	1.1000	1.1000
0.300	570.500	-0.250	370.151	2.325	0.3000	1.1328	1.1141	1.1000	1.1000	1.1000
0.333	569.000	-0.250	401.221	2.579	0.3330	1.1777	1.1777	1.1777	1.1777	1.1777
0.417	753.000	-0.250	0.000	2.579	0.4170	1.0452	1.0452	1.0452	1.0452	1.0452
0.710	765.500	-0.050	0.000	4.744	0.7100	1.0452	1.0452	1.0452	1.0452	1.0452
0.917	753.500	-0.050	0.000	5.670	0.9170	1.0452	1.0452	1.0452	1.0452	1.0452
1.417	713.500	-0.050	0.000	8.753	1.4170	1.0452	1.0452	1.0452	1.0452	1.0452
2.833	613.000	0.200	0.000	16.549	2.8330	1.0452	1.0452	1.0452	1.0452	1.0452
3.417	586.000	0.200	0.000	18.630	3.4170	1.0452	1.0452	1.0452	1.0452	1.0452
4.000	553.000	0.200	0.000	21.018	4.0000	1.0452	1.0452	1.0452	1.0452	1.0452
4.033	553.000	0.200	367.314	20.728	4.0330	1.0222	1.0222	1.0222	1.0222	1.0222
4.100	530.000	0.200	618.830	21.810	4.1000	1.0354	1.0354	1.0354	1.0354	1.0354
4.133	524.000	0.200	381.813	21.961	4.1330	1.0308	1.0308	1.0308	1.0308	1.0308
4.333	527.500	0.200	0.000	21.961	4.3330	1.0308	1.0308	1.0308	1.0308	1.0308
4.417	783.000	0.200	0.000	21.961	4.4170	1.0308	1.0308	1.0308	1.0308	1.0308
4.917	746.000	0.200	0.000	24.819	4.9170	1.0308	1.0308	1.0308	1.0308	1.0308
12.380	399.000	0.650	0.000	51.600	12.3800	1.0308	1.0308	1.0308	1.0308	1.0308
13.420	401.500	0.750	0.000	51.419	13.4200	1.0308	1.0308	1.0308	1.0308	1.0308
15.300	402.500	0.850	0.000	51.419	15.3000	1.0308	1.0308	1.0308	1.0308	1.0308
15.920	571.000	1.900	0.000	53.641	15.9200	1.0308	1.0308	1.0308	1.0308	1.0308
15.930	567.000	1.950	404.461	54.173	15.9300	1.0308	1.0308	1.0308	1.0308	1.0308
15.980	564.500	1.900	105.339	54.166	15.9800	1.0308	1.0308	1.0308	1.0308	1.0308
16.030	561.500	1.900	105.250	54.166	16.0300	1.0308	1.0308	1.0308	1.0308	1.0308
16.110	975.000	7.250	0.000	55.132	16.1100	10.1540	10.1540	10.1540	10.1540	10.1540
16.420	144.000	1.100	0.000	60.819	16.4200	10.1540	10.1540	10.1540	10.1540	10.1540
19.170	165.000	1.450	0.000	61.793	19.1700	10.1540	10.1540	10.1540	10.1540	10.1540
19.430	402.500	0.300	0.000	62.414	19.4300	9.6020	9.6020	9.6020	9.6020	9.6020
19.530	196.000	0.450	0.000	62.377	19.5300	9.6020	9.6020	9.6020	9.6020	9.6020
19.540	141.000	0.150	0.000	62.377	19.5400	9.6020	9.6020	9.6020	9.6020	9.6020
19.550	141.000	0.150	0.000	62.377	19.5500	9.6020	9.6020	9.6020	9.6020	9.6020
19.560	141.000	0.150	0.000	62.377	19.5600	9.6020	9.6020	9.6020	9.6020	9.6020
19.570	141.000	0.150	0.000	62.377	19.5700	9.6020	9.6020	9.6020	9.6020	9.6020
19.580	141.000	0.150	0.000	62.377	19.5800	9.6020	9.6020	9.6020	9.6020	9.6020
19.590	141.000	0.150	0.000	62.377	19.5900	9.6020	9.6020	9.6020	9.6020	9.6020
19.600	141.000	0.150	0.000	62.377	19.6000	9.6020	9.6020	9.6020	9.6020	9.6020
19.610	141.000	0.150	0.000	62.377	19.6100	9.6020	9.6020	9.6020	9.6020	9.6020
19.620	141.000	0.150	0.000	62.377	19.6200	9.6020	9.6020	9.6020	9.6020	9.6020
19.630	141.000	0.150	0.000	62.377	19.6300	9.6020	9.6020	9.6020	9.6020	9.6020
19.640	141.000	0.150	0.000	62.377	19.6400	9.6020	9.6020	9.6020	9.6020	9.6020
19.650	141.000	0.150	0.000	62.377	19.6500	9.6020	9.6020	9.6020	9.6020	9.6020
19.660	141.000	0.150	0.000	62.377	19.6600	9.6020	9.6020	9.6020	9.6020	9.6020
19.670	141.000	0.150	0.000	62.377	19.6700	9.6020	9.6020	9.6020	9.6020	9.6020
19.680	141.000	0.150	0.000	62.377	19.6800	9.6020	9.6020	9.6020	9.6020	9.6020
19.690	141.000	0.150	0.000	62.377	19.6900	9.6020	9.6020	9.6020	9.6020	9.6020
19.700	141.000	0.150	0.000	62.377	19.7000	9.6020	9.6020	9.6020	9.6020	9.6020
19.710	141.000	0.150	0.000	62.377	19.7100	9.6020	9.6020	9.6020	9.6020	9.6020
19.720	141.000	0.150	0.000	62.377	19.7200	9.6020	9.6020	9.6020	9.6020	9.6020
19.730	141.000	0.150	0.000	62.377	19.7300	9.6020	9.6020	9.6020	9.6020	9.6020
19.740	141.000	0.150	0.000	62.377	19.7400	9.6020	9.6020	9.6020	9.6020	9.6020
19.750	141.000	0.150	0.000	62.377	19.7500	9.6020	9.6020	9.6020	9.6020	9.6020
19.760	141.000	0.150	0.000	62.377	19.7600	9.6020	9.6020	9.6020	9.6020	9.6020
19.770	141.000	0.150	0.000	62.377	19.7700	9.6020	9.6020	9.6020	9.6020	9.6020
19.780	141.000	0.150	0.000	62.377	19.7800	9.6020	9.6020	9.6020	9.6020	9.6020
19.790	141.000	0.150	0.000	62.377	19.7900	9.6020	9.6020	9.6020	9.6020	9.6020
19.800	141.000	0.150	0.000	62.377	19.8000	9.6020	9.6020	9.6020	9.6020	9.6020
19.810	141.000	0.150	0.000	62.377	19.8100	9.6020	9.6020	9.6020	9.6020	9.6020
19.820	141.000	0.150	0.000	62.377	19.8200	9.6020	9.6020	9.6020	9.6020	9.6020
19.830	141.000	0.150	0.000	62.377	19.8300	9.6020	9.6020	9.6020	9.6020	9.6020
19.840	141.000	0.150	0.000	62.377	19.8400	9.6020	9.6020	9.6020	9.6020	9.6020
19.850	141.000	0.150	0.000	62.377	19.8500	9.6020	9.6020	9.6020	9.6020	9.6020
19.860	141.000	0.150	0.000	62.377	19.8600	9.6020	9.6020	9.6020	9.6020	9.6020
19.870	141.000	0.150	0.000	62.377	19.8700	9.6020	9.6020	9.6020	9.6020	9.6020
19.880	141.000	0.150	0.000	62.377	19.8800	9.6020	9.6020	9.6020	9.6020	9.6020
19.890	141.000	0.150	0.000	62.377	19.8900	9.6020	9.6020	9.6020	9.6020	9.6020
19.900	141.000	0.150	0.000	62.377	19.9000	9.6020	9.6020	9.6020	9.6020	9.6020
19.910	141.000	0.150	0.000	62.377	19.9100	9.6020	9.6020	9.6020	9.6020	9.6020
19.920	141.000	0.150	0.000	62.377	19.9200	9.6020	9.6020	9.6020	9.6020	9.6020
19.930	141.000	0.150	0.000	62.377	19.9300	9.6020	9.6020	9.6020	9.6020	9.6020
19.940	141.000	0.150	0.000	62.377	19.9400	9.6020	9.6020	9.6020	9.6020	9.6020
19.950	141.000	0.150	0.000	62.377	19.9500	9.6020	9.6020	9.6020	9.6020	9.6020
19.960	141.000	0.150	0.000	62.377	19.9600	9.6020	9.6020	9.6020	9.6020	9.6020
19.970	141.000	0.150	0.000	62.377	19.9700	9.6020	9.6020	9.6020	9.6020	9.6020
19.980	141.000	0.150	0.000	62.377	19.9800	9.6020	9.6020	9.6020	9.6020	9.6020
19.990	141.000	0.150	0.000	62.377	19.9900	9.6020	9.6020	9.6020	9.6020	9.6020
20.000	141.000	0.150	0.000	62.377	20.0000	9.6020	9.6020	9.6020	9.6020	9.6020

METHANE HYDRATE FORMATION RUN # 2
 DATE RUN STARTED:10-25-1987
 DATE RUN ENDED:10-27-1987
 GRAMS OF H2O= 861.100
 GRAMS OF SAND= 881.000
 HEIGHT OF THE CORE= 29.21CM.
 ROOM TEMPERATURE= 20.8000DEG.C
 TEMP.OF GAS LEAVING WET TEST METER= 16.8000DEG.C
 BAROMETRIC PRESSURE= 743.300MM.HG
 VAP.PRESSURE OF WATER AT TWIM= 14.071MM.HG
 ICE TO SAND VOL.RATIO= 2.761
 ICE TO SAND MASS RATIO= 0.977
 PERCENTAGE VOIDS IN THE CORE= 45.983
 G/MOL.METHANE FOR 100 PERCENT CONVERSION= 8.312421
 HYDRATE FORMATION RUN INPUT DATA

TIME (HR)	P1 (PSIA)	P3 (PSIA)	PL (PSIA)	PM (PSIA)	PR (PSIA)	T1RTD (DEG.C)	T2RTD (DEG.C)	FIREAD	WVTH (LIT)
0.00	750.00	750.00	749.00	750.00	741.00	-0.60	-0.60	0.00	0.00
0.03	738.00	737.00	737.00	735.00	730.00	-0.60	-0.60	3.90	0.62
0.07	727.00	726.00	725.00	727.00	720.00	-0.60	-0.60	4.10	1.40
0.10	718.00	718.00	715.00	716.00	709.00	-0.50	-0.60	4.50	2.00
0.17	690.00	690.00	689.00	690.00	688.00	-0.50	-0.60	7.80	5.20
0.18	678.00	678.00	678.00	676.00	678.00	-0.50	-0.60	6.90	6.31
0.35	668.00	668.00	667.00	668.00	665.00	-0.50	-0.60	6.80	7.39
2.07	438.00	438.00	435.00	437.00	438.00	-0.40	-0.30	0.00	0.00
2.12	610.00	610.00	609.00	611.00	467.00	-0.40	-0.30	0.00	7.39
2.19	625.00	625.00	626.00	628.00	526.00	-0.40	-0.30	4.10	8.72
2.22	623.00	623.00	623.00	625.00	539.00	-0.40	-0.30	3.80	9.06
2.29	622.00	622.00	619.00	621.00	538.00	-0.40	-0.30	3.70	9.41
2.32	597.00	597.00	595.00	597.00	560.00	-0.40	-0.30	11.60	12.54
2.34	581.00	581.00	580.00	583.00	561.00	-0.40	-0.30	10.90	14.10
2.36	569.00	569.00	567.00	568.00	561.00	-0.40	-0.30	9.80	15.72
2.39	660.00	660.00	661.00	663.00	571.00	-0.40	-0.30	0.00	16.11
6.39	556.00	556.00	445.00	431.00	441.00	-0.20	-0.60	0.00	16.11
6.41	543.00	543.00	461.00	437.00	446.00	-0.20	-0.60	5.90	17.34
6.44	532.00	543.00	468.00	440.00	450.00	-0.20	-0.60	5.60	18.30
6.51	524.00	524.00	471.00	442.00	452.00	-0.20	-0.60	5.50	19.14
6.52	508.00	508.00	475.00	445.00	455.00	-0.20	-0.60	14.40	21.10
6.56	480.00	480.00	474.00	445.00	455.00	-0.20	-0.60	17.60	24.20
6.79	650.00	650.00	543.00	492.00	519.00	-0.20	-0.60	0.00	0.00
17.90	392.00	393.00	390.00	407.00	392.00	0.10	0.20	0.00	0.00
18.00	696.00	697.00	695.00	421.00	572.00	6.80	5.90	0.00	0.00
20.25	576.00	575.00	562.00	520.00	525.00	3.00	1.10	0.00	24.20
20.36	558.00	558.00	562.00	519.00	519.00	2.30	0.70	6.00	26.41
20.39	554.00	555.00	562.00	519.00	518.00	2.30	0.70	6.00	27.22
20.43	550.00	551.00	562.00	519.00	517.00	2.30	0.70	6.00	28.35
20.50	549.00	549.00	562.00	518.00	516.00	2.30	0.70	0.00	0.00
20.68	792.00	792.00	589.00	516.00	583.00	2.70	1.20	0.00	0.00
29.80	718.00	718.00	662.00	469.00	706.00	-0.40	-0.70	0.00	28.50
29.83	714.00	713.00	662.00	469.00	706.00	-0.40	-0.70	6.00	30.10
29.87	704.00	703.00	662.00	469.00	706.00	-0.40	-0.70	6.10	31.72
29.90	696.00	696.00	662.00	469.00	706.00	-0.40	-0.70	5.90	32.99
29.95	692.00	692.00	662.00	469.00	706.00	-0.40	-0.70	0.00	0.00
42.03	669.00	670.00	653.00	466.00	479.00	-0.50	-0.70	0.00	0.00
46.03	664.00	665.00	652.00	466.00	679.00	-0.70	-0.90	0.00	32.99
42.05	650.00	652.00	652.00	466.00	679.00	-1.50	-1.40	27.90	34.84
42.08	647.00	648.00	652.00	466.00	679.00	-0.30	-1.00	28.80	35.73
42.12	645.00	645.00	652.00	466.00	679.00	-0.50	-0.80	30.00	36.62
45.20	600.00	600.00	652.00	466.00	679.00	-0.50	-0.80	0.00	42.12

RESULTS OF HYDRATE RUN

TIME (HR)	PRAR (PSIA)	TBAR (DEG.C)	QBAR (CC/MIN)	CONV (%)	TIME	GMOLG	GMOLC	GMOLIN	GMLOUT	GMOLH	CONV
0.000	750.000	-0.100	0.000	0.000	0.0000	4.2788	4.2788	0.0000	0.0000	0.0000	0.0000
0.033	737.500	-0.100	173.693	0.602	0.0330	4.2575	4.2075	0.0049	0.0262	0.0500	0.6017
0.066	726.500	-0.100	212.896	1.022	0.0660	4.2297	4.1448	0.0051	0.0329	0.0850	1.0222
0.099	718.000	-0.050	173.149	1.378	0.0990	4.2100	4.0955	0.0056	0.0253	0.1145	1.3775
0.166	690.000	-0.050	810.547	1.792	0.1657	4.0848	3.9358	0.0097	0.1350	0.1490	1.7919
0.182	678.000	-0.050	310.393	2.155	0.1824	4.0465	3.8673	0.0086	0.0468	0.1792	2.1554
0.350	668.000	-0.050	302.607	2.395	0.3500	4.0094	3.8103	0.0085	0.0456	0.1991	2.3954
2.070	438.000	0.150	0.000	18.200	2.0700	4.0094	2.4965	0.0000	0.0000	1.5129	18.2002
2.120	610.000	0.150	0.000	18.200	2.1200	4.9898	3.4769	0.9804	0.0000	1.5129	18.2002
2.190	625.000	0.150	342.865	16.558	2.1900	4.9388	3.5624	0.0051	0.0561	1.3764	16.5581
2.220	623.000	0.150	106.830	16.580	2.2200	4.9292	3.5510	0.0047	0.0143	1.3782	16.5796
2.290	622.000	0.150	108.496	16.526	2.2900	4.9190	3.5453	0.0046	0.0148	1.3737	16.5260
2.320	597.000	0.150	820.491	16.826	2.3200	4.8014	3.4028	0.0144	0.1320	1.3986	16.8256
2.340	581.000	0.150	444.611	17.294	2.3400	4.7492	3.3116	0.0136	0.0658	1.4376	17.2943
2.360	569.000	0.150	451.123	17.442	2.3600	4.6931	3.2432	0.0122	0.0683	1.4498	17.4418
2.390	660.000	0.150	0.000	17.442	2.3900	5.2118	3.7619	0.5187	0.0000	1.4498	17.4418
6.390	556.000	0.100	0.000	24.566	6.3900	5.2118	3.1697	0.0000	0.0000	2.0420	24.5662
6.410	543.000	0.100	331.780	24.922	6.4100	5.1672	3.0956	0.0073	0.0519	2.0716	24.9219
6.440	537.500	0.100	265.886	24.896	6.4400	5.1337	3.0642	0.0070	0.0405	2.0694	24.8958
6.510	524.000	0.100	236.832	25.478	6.5100	5.1051	2.9873	0.0068	0.0354	2.1178	25.4778
6.523	508.000	0.100	563.529	25.796	6.5230	5.0404	2.8961	0.0179	0.0827	2.1443	25.7961
6.560	480.000	0.100	855.222	26.407	6.5600	4.9315	2.7364	0.0219	0.1308	2.1950	26.4069
6.790	650.000	0.100	0.000	26.407	6.7900	5.9006	3.7056	0.9692	0.0000	2.1950	26.4069
17.900	392.500	0.650	0.000	44.121	17.9000	5.9006	2.2331	0.0000	0.0000	3.6675	44.1211
18.000	696.500	6.850	0.000	44.121	18.0000	7.5425	3.8750	1.6419	0.0000	3.6675	44.1211
20.250	575.500	2.550	0.000	51.619	20.2500	7.5425	3.2517	0.0000	0.0000	4.2908	51.6189
20.360	558.000	2.000	564.057	51.701	20.3600	7.4568	3.1591	0.0075	0.0932	4.2976	51.7010
20.393	554.500	2.000	233.228	51.618	20.3930	7.4301	3.1393	0.0075	0.0342	4.2907	51.6182
20.430	550.500	2.000	308.846	51.407	20.4300	7.3899	3.1167	0.0075	0.0477	4.2732	51.4070
20.500	549.000	2.000	0.000	51.509	20.5000	7.3839	3.1082	0.0000	0.0000	4.2817	51.5092
20.680	792.000	2.450	0.000	51.509	20.6800	8.7583	4.4766	1.3644	0.0000	4.2817	51.5092
29.800	718.000	-0.050	0.000	56.094	29.8000	8.7583	4.0955	0.0000	0.0000	4.6628	56.0942
29.833	713.500	-0.050	419.910	55.681	29.8330	8.6983	4.0698	0.0075	0.0675	4.6284	55.6809
29.870	703.500	-0.050	425.334	55.636	29.8700	8.6375	4.0128	0.0076	0.0683	4.6247	55.6364
29.900	696.000	-0.050	341.232	55.595	29.9000	8.5913	3.9700	0.0073	0.0536	4.6213	55.5949
29.950	692.000	-0.050	0.000	55.869	29.9500	8.5913	3.9472	0.0000	0.0000	4.6441	55.8694
42.030	669.500	-0.100	0.000	57.405	42.0300	8.5913	3.8196	0.0000	0.0000	4.7717	57.4049
46.030	664.500	-0.300	0.000	57.715	46.0300	8.5913	3.7938	0.0000	0.0000	4.7975	57.7147
42.050	651.000	-0.950	631.630	58.014	42.0500	8.5480	3.7256	0.0347	0.0780	4.8224	58.0140
42.083	647.500	-0.150	411.049	58.365	42.0830	8.5463	3.6947	0.0358	0.0375	4.8515	58.3650
42.120	645.000	-0.150	419.413	58.534	42.1200	8.5461	3.6805	0.0373	0.0375	4.8656	58.5340
45.200	600.000	-0.150	0.000	58.832	45.2000	8.3141	3.4237	0.0000	0.2320	4.8904	58.8323

METHANE HYDRATE FORMATION RUN # 3
 DATE RUN STARTED:10-29-1987
 DATE RUN ENDED:10-31-1987
 GRAMS OF H2O- 726.000
 GRAMS OF SAND- 710.600
 HEIGHT OF THE CORE- 28.60CM.
 ROOM TEMPERATURE- 21.0000DEG.C
 TEMP.OF GAS LEAVING WET TEST METER- 16.5000DEG.C
 BAROMETRIC PRESSURE- 744.300MM.HG
 VAP.PRESSURE OF WATER AT TWIM- 14.070MM.HG
 ICE TO SAND VOL.RATIO- 2.886
 ICE TO SAND MASS RATIO- 1.022
 PERCENTAGE VOIDS IN THE CORE- 54.022
 G/MOL.METHANE FOR 100 PERCENT CONVERSION- 7.088261
 HYDRATE FORMATION RUN INPUT DATA

TIME (HR)	P1 (PSIA)	P3 (PSIA)	PL (PSIA)	PM (PSIA)	PR (PSIA)	T1RTD (DEG.C)	T2RTD (DEG.C)	FIREAD	VWTH (LIT)
0.00	696.00	696.00	694.00	694.00	696.00	-0.70	-0.50	0.00	0.00
0.17	664.00	664.00	662.00	662.00	664.00	-0.60	-0.50	0.00	0.00
0.33	644.00	644.00	643.00	643.00	645.00	-0.60	-0.50	0.00	1.67
0.37	637.00	637.00	636.00	636.00	636.00	-0.70	-0.80	19.10	2.30
0.40	636.00	636.00	635.00	635.00	636.00	-0.80	-0.90	18.50	2.70
0.43	635.00	635.00	634.00	634.00	636.00	-0.70	-0.40	18.20	2.91
0.45	736.00	735.00	735.00	735.00	737.00	-0.70	-0.50	0.00	0.00
1.07	707.00	706.00	706.00	705.00	707.00	-0.70	-0.50	0.00	0.00
1.57	693.00	692.00	692.00	691.00	693.00	-0.60	-0.30	0.00	0.00
2.07	667.00	666.00	656.00	655.00	655.00	-0.60	-0.40	0.00	2.91
2.10	651.00	651.00	650.00	649.00	672.00	-0.60	-0.50	20.70	4.96
2.14	648.00	648.00	648.00	647.00	672.00	-0.60	-0.50	20.70	5.27
2.17	644.00	644.00	644.00	644.00	672.00	-0.60	-0.50	19.60	5.93
2.20	756.00	754.00	754.00	754.00	698.00	-0.70	-0.80	0.00	0.00
3.59	717.00	716.00	716.00	716.00	717.00	-0.50	-0.40	0.00	0.00
5.17	684.00	684.00	694.00	713.00	686.00	-0.40	-0.70	0.00	0.00
14.92	407.00	404.00	402.00	402.00	402.00	-0.40	-0.70	0.00	5.93
14.95	402.00	404.00	400.00	399.00	400.00	-0.10	-0.30	17.80	6.30
14.98	397.00	397.00	398.00	396.00	397.00	-0.10	-0.30	17.80	6.57
15.02	395.00	395.00	395.00	395.00	395.00	-0.10	-0.30	19.90	7.41
15.65	776.00	776.00	774.00	762.00	657.00	3.30	-0.30	0.00	0.00
20.04	678.00	680.00	678.00	670.00	664.00	3.20	2.60	0.00	0.00
21.85	640.00	640.00	637.00	641.00	492.00	0.30	-1.40	0.00	7.41
21.89	630.00	630.00	627.00	641.00	492.00	0.20	-1.30	19.90	9.39
21.92	623.00	623.00	620.00	641.00	491.00	0.20	-1.30	19.80	10.48
21.95	614.00	614.00	611.00	641.00	491.00	0.20	-1.30	19.70	11.92
21.98	604.00	604.00	603.00	641.00	491.00	0.20	-1.30	19.60	13.51
22.20	752.00	752.00	749.00	640.00	488.00	-0.40	-7.41	0.00	0.00
23.45	743.00	745.00	744.00	717.00	696.00	-0.50	-0.40	0.00	0.00
0.00	676.00	676.00	676.00	708.00	660.00	5.60	2.50	0.00	13.51
26.73	670.00	670.00	668.00	708.00	666.00	5.20	2.50	20.50	16.30
26.77	665.00	665.00	663.00	708.00	661.00	5.10	2.50	17.50	18.30
26.83	661.00	661.00	659.00	708.00	656.00	5.10	2.40	18.20	18.70
26.84	655.00	655.00	657.00	708.00	656.00	5.10	2.40	18.50	19.30
27.08	805.00	804.00	802.00	708.00	657.00	7.20	2.30	0.00	0.00
41.08	701.00	701.00	699.00	659.00	669.00	2.40	2.30	0.00	0.00
44.58	676.00	676.00	675.00	611.00	569.00	-0.70	-2.40	0.00	19.30
44.61	667.00	667.00	664.00	569.00	0.00	-0.60	-2.20	18.82	23.50
44.65	657.00	656.00	654.00	610.00	569.00	-0.70	-2.20	19.40	24.80
44.68	650.00	649.00	649.00	610.00	569.00	-0.70	-2.50	19.80	25.70
47.36	648.00	648.00	646.00	612.00	563.00	-1.60	-2.10	0.00	0.00

RESULTS OF HYDRATE RUN

TIME	GMOLO	GMOLG	GMOLIN	GMOLOT	GMOLEH	CONV	TIME (HR)	PRAR (PSIA)	TRAR (DEG.C)	QBAR (CC/MIN)	CONV (%)
0.0000	4.5135	4.5135	0.0000	0.0000	0.0000	0.0000	0.000	696.000	-0.100	0.000	0.000
0.1670	4.5135	4.3052	0.0000	0.0000	0.2083	-2.9723	0.167	664.000	-0.050	0.000	2.972
0.3330	4.4429	4.1755	0.0000	0.0706	0.2674	3.8151	0.333	644.000	-0.050	0.000	3.815
0.3670	4.4400	4.1331	0.0238	0.0266	0.3069	4.3785	0.367	637.000	-0.250	282.359	4.378
0.3990	4.4461	4.1282	0.0230	0.0169	0.3179	4.5366	0.399	636.000	-0.350	223.695	4.537
0.4320	4.4599	4.1172	0.0226	0.0089	0.3427	4.8902	0.432	635.000	-0.050	176.598	4.890
0.4500	5.1124	4.7696	0.6525	0.0000	0.3427	4.8902	0.450	735.500	-0.100	0.000	4.890
1.0700	5.1124	4.5816	0.0000	0.0000	0.5308	7.5736	1.070	706.500	-0.100	0.000	7.574
1.5700	5.1124	4.4883	0.0000	0.0000	0.6240	8.9042	1.570	692.500	0.050	0.000	8.904
2.0700	5.1124	4.3206	0.0000	0.0000	0.7918	11.2975	2.070	666.500	0.000	0.000	11.297
2.1030	5.0514	4.2209	0.0258	0.0867	0.8305	11.8509	2.103	651.000	-0.050	629.875	11.851
2.1400	5.0641	4.2014	0.0258	0.0131	0.8626	12.3089	2.140	648.000	-0.050	217.711	12.309
2.1700	5.0606	4.1755	0.0244	0.0279	0.8851	12.6287	2.170	644.000	-0.050	292.950	12.629
2.2000	5.7838	4.8988	0.7233	0.0000	0.8851	12.6287	2.200	755.000	-0.250	0.000	12.629
3.5900	5.7838	4.6439	0.0000	0.0000	1.1400	16.2660	3.590	716.500	0.050	0.000	16.266
5.1700	5.7838	4.4349	0.0000	0.0000	1.3490	19.2485	5.170	684.000	-0.050	0.000	19.248
14.9200	5.7838	2.6291	0.0000	0.0000	3.1547	45.0139	14.920	405.500	-0.050	0.000	45.014
14.9500	5.7903	2.6096	0.0221	0.0156	3.1807	45.3857	14.950	403.000	0.300	211.710	45.386
14.9800	5.8011	2.5707	0.0221	0.0114	3.2303	46.0932	14.980	397.000	0.300	188.022	46.093
15.0200	5.7903	2.5578	0.0248	0.0355	3.2325	46.1245	15.020	395.000	0.300	137.679	46.124
15.6500	8.2264	4.9939	2.4361	0.0000	3.2325	46.1245	15.650	776.000	2.000	0.000	46.124
20.0400	8.2264	4.3475	0.0000	0.0000	3.8789	55.3472	20.040	679.000	3.400	0.000	55.347
21.8500	8.2264	4.1496	0.0000	0.0000	4.0768	58.1716	21.850	640.000	-0.050	0.000	58.172
21.8900	8.1674	4.0847	0.0248	0.0837	4.0827	58.2555	21.890	630.000	-0.050	607.717	58.256
21.9200	8.1460	4.0393	0.0246	0.0461	4.1066	58.5970	21.920	623.000	-0.050	396.201	58.597
21.9500	8.1096	3.9810	0.0245	0.0609	4.1286	58.9106	21.950	614.000	-0.050	478.410	58.911
21.9800	8.0668	3.9162	0.0244	0.0672	4.1506	59.2245	21.980	604.000	-0.050	513.245	59.224
22.2000	9.0870	4.9364	1.0202	0.0000	4.1506	59.2245	22.200	752.000	-3.405	0.000	59.224
23.4500	9.0870	4.8221	0.0000	0.0000	4.2649	60.8551	23.450	744.000	0.050	0.000	60.855
0.0000	9.0870	4.3104	0.0000	0.0000	4.7766	68.1569	0.000	676.000	4.550	0.000	68.157
26.7330	8.9945	4.2752	0.0255	0.1180	4.7193	67.3396	26.733	670.000	4.350	803.769	67.340
26.7700	8.9318	4.2441	0.0218	0.0846	4.6877	66.8880	26.770	665.000	4.300	595.727	66.888
26.8300	8.9375	4.2193	0.0226	0.0169	4.7182	67.3232	26.830	661.000	4.250	221.604	67.323
26.8400	8.9351	4.1810	0.0230	0.0254	4.7541	67.9361	26.840	655.000	4.250	271.071	67.936
27.0800	9.8710	5.1168	0.9358	0.0000	4.7541	67.8361	27.080	804.500	5.250	0.000	67.936
41.0800	9.8710	4.4973	0.0000	0.0000	5.3736	76.6759	41.080	701.000	2.850	0.000	76.676
44.5800	9.8710	4.3991	0.0000	0.0000	5.4719	79.0775	44.580	676.000	-1.050	0.000	79.078
44.6100	9.7168	4.3381	0.0234	0.1776	5.3787	76.7476	44.610	667.000	-0.900	1126.054	76.748
44.6500	9.6860	4.2706	0.0241	0.0550	5.4154	77.2709	44.650	656.500	-0.950	443.157	77.271
44.6830	9.6726	4.2274	0.0246	0.0381	5.4451	77.6960	44.683	649.500	-1.100	351.194	77.696
47.3600	9.6726	4.2215	0.0000	0.0000	5.4510	77.7799	47.360	645.000	-1.350	0.000	77.780

METHANE HYDRATE FORMATION RUN # 4
 DATE RUN STARTED: 11- 2-1987
 DATE RUN ENDED: 11- 4-1987
 GRAMS OF H₂O- 719.800
 GRAMS OF SAND- 714.800
 HEIGHT OF THE CORE- 28.44CM.
 ROOM TEMPERATURE- 20.9000DEG.C
 TEMP.OF GAS LEAVING WET TEST METER- 16.5000DEG.C
 BAROMETRIC PRESSURE- 744.400MM.HG
 VAP.PRESSURE OF WATER AT TWT- 14.078MM.HG
 ICE TO SAND VOL.RATIO- 2.844
 ICE TO SAND MASS RATIO- 1.007
 PERCENTAGE VOIDS IN THE CORE- 53.987
 GMOL.METHANE FOR 100 PERCENT CONVERSION- 6.948411
 HYDRATE FORMATION RUN INPUT DATA

TIME (HR)	P1 (PSIA)	P3 (PSIA)	PL (PSIA)	PM (PSIA)	PR (PSIA)	T1RTD (DEG.C)	T2RTD (DEG.C)	FIREAD	WVTH (LIT)
0.00	749.00	747.00	748.00	746.00	748.00	-2.20	-1.60	0.00	0.00
0.03	728.00	726.00	727.00	725.00	727.00	-2.10	-1.10	18.00	1.68
0.07	719.00	718.00	719.00	717.00	719.00	-2.10	-1.00	17.90	2.51
0.10	712.00	711.00	712.00	709.00	711.00	-1.70	-0.80	17.80	3.49
0.13	706.00	705.00	706.00	704.00	706.00	-1.60	-0.70	17.80	4.14
0.23	769.00	768.00	769.00	767.00	770.00	-1.50	-0.70	0.00	4.30
4.02	607.00	607.00	621.00	607.00	608.00	-0.70	-0.30	0.00	4.30
4.05	602.00	601.00	621.00	602.00	601.00	-0.80	-0.50	19.80	5.09
4.08	599.00	598.00	621.00	599.00	599.00	-0.80	-0.30	19.80	5.82
4.11	594.00	593.00	620.00	594.00	594.00	-0.80	-0.60	19.80	6.54
4.15	589.00	589.00	620.00	589.00	589.00	-1.10	-0.50	19.90	7.52
4.21	722.00	721.00	622.00	721.00	721.00	-3.20	-0.50	0.00	0.00
7.41	602.00	602.00	603.00	601.00	689.00	-0.80	-0.70	0.00	7.52
7.45	596.00	596.00	591.00	593.00	689.00	-0.80	-0.50	15.00	9.22
7.48	590.00	590.00	588.00	587.00	689.00	-0.70	-0.30	19.80	10.01
7.55	584.00	582.00	583.00	582.00	689.00	-0.70	-0.50	19.50	10.77
7.58	580.00	579.00	581.00	580.00	688.00	-0.80	-0.30	19.50	11.32
7.80	888.00	886.00	872.00	869.00	756.00	-1.00	-0.80	0.00	0.00
16.63	693.00	694.00	696.00	698.00	769.00	0.50	-0.40	0.00	11.32
17.05	592.00	592.00	597.00	596.00	735.00	0.50	-0.40	0.00	24.13
17.08	587.00	587.00	594.00	593.00	736.00	1.10	-0.40	19.80	25.04
17.12	583.00	583.00	591.00	590.00	735.00	1.00	-0.40	19.60	25.91
17.15	580.00	580.00	588.00	586.00	736.00	1.30	-0.40	19.60	26.60
17.25	754.00	751.00	751.00	753.00	744.00	2.40	-0.30	0.00	0.00
19.75	701.00	700.00	699.00	699.00	732.00	1.40	-0.40	0.00	0.00
23.32	607.00	607.00	607.00	618.00	728.00	0.20	3.10	0.00	26.60
23.35	599.00	599.00	605.00	615.00	727.00	2.20	4.50	20.00	27.72
23.39	594.00	593.00	601.00	611.00	727.00	2.10	4.40	19.90	28.47
23.42	589.00	588.00	595.00	604.00	726.00	2.10	4.30	19.90	29.08
23.45	584.00	583.00	591.00	597.00	726.00	2.50	4.30	19.80	29.93
23.64	750.00	750.00	739.00	749.00	735.00	2.70	6.60	0.00	0.00
27.64	649.00	648.00	628.00	648.00	717.00	0.90	-0.30	0.00	29.93
27.70	602.00	601.00	613.00	602.00	717.00	0.80	-0.60	0.00	39.00
27.74	599.00	598.00	600.00	598.00	717.00	0.80	-0.50	19.30	39.70
27.77	593.00	593.00	591.00	593.00	717.00	0.80	-0.60	19.10	40.63
27.80	589.00	588.00	586.00	590.00	717.00	0.70	-0.50	18.90	41.42
28.00	842.00	842.00	803.00	833.00	756.00	2.20	0.80	0.00	0.00
32.39	752.00	751.00	689.00	751.00	709.00	1.10	-0.30	0.00	0.00
32.62	846.00	845.00	758.00	841.00	730.00	2.10	0.70	0.00	0.00
43.87	706.00	706.00	604.00	703.00	688.00	-0.30	0.30	0.00	41.42
44.61	600.00	600.00	606.00	600.00	687.00	-0.70	-0.30	0.00	55.62
44.64	596.00	585.00	606.00	596.00	687.00	1.00	-0.40	19.70	56.56
44.68	592.00	591.00	606.00	592.00	687.00	-0.50	-0.40	19.60	57.42
44.71	587.00	587.00	606.00	587.00	687.00	-0.60	-0.50	19.30	58.16
44.74	584.00	583.00	606.00	584.00	687.00	-0.60	-0.40	19.00	59.01

RESULTS OF HYDRATE RUN

TIME (HR)	FBAR (PSIA)	TBAR (DEG.C)	QBAR (CC/MIN)	CONV (%)	TIME	GMOLG	GMOLG	GMOLIN	GMOLUT	GMOLN	CONV
0.000	748.000	-1.400	0.000	0.000	0.0000	4.8559	4.8559	0.0000	0.0000	0.0000	0.0000
0.033	727.000	-1.100	523.462	1.337	0.0330	4.8072	4.7143	0.0224	0.0710	0.0929	1.3368
0.066	718.500	-1.050	321.395	1.958	0.0660	4.7944	4.6584	0.0223	0.0351	0.1360	1.9578
0.099	711.500	-0.750	356.234	2.406	0.0990	4.7751	4.6079	0.0221	0.0414	0.1672	2.4064
0.132	705.500	-0.650	278.055	2.913	0.1320	4.7698	4.5674	0.0221	0.0275	0.2024	2.9129
0.232	768.500	-0.600	0.000	2.913	0.2320	5.1767	4.9743	0.4069	0.0000	0.2024	2.9129
4.015	607.000	0.000	0.000	18.082	4.0150	5.1767	3.9203	0.0000	0.0000	1.2564	18.0815
4.048	601.500	-0.150	325.162	18.436	4.0480	5.1679	3.8869	0.0246	0.0334	1.2810	18.4358
4.081	598.500	-0.050	310.947	18.645	4.0810	5.1617	3.8661	0.0246	0.0309	1.2956	18.6454
4.115	593.500	-0.200	308.578	18.996	4.1150	5.1559	3.8360	0.0246	0.0304	1.3199	18.9963
4.150	589.000	-0.300	370.871	19.155	4.1500	5.1392	3.8083	0.0248	0.0414	1.3309	19.1547
4.210	721.500	-1.350	0.000	19.155	4.2100	6.0139	4.6830	0.8747	0.0000	1.3309	19.1547
7.410	602.000	-0.250	0.000	30.544	7.4100	6.0139	3.8916	0.0000	0.0000	2.1223	30.5440
7.450	596.000	-0.150	507.290	30.357	7.4500	5.9607	3.8514	0.0187	0.0719	2.1093	30.3565
7.483	590.000	0.000	325.162	30.818	7.4830	5.9519	3.8105	0.0246	0.0334	2.1414	30.8184
7.545	583.000	-0.100	315.963	31.336	7.5450	5.9441	3.7667	0.0243	0.0321	2.1773	31.3358
7.580	579.500	-0.050	266.213	31.686	7.5800	5.9451	3.7434	0.0243	0.0233	2.2016	31.6856
7.795	887.000	-0.400	0.000	31.686	7.7950	7.9388	5.7371	1.9937	0.0000	2.2016	31.6856
16.630	693.500	0.550	0.000	49.922	16.6300	7.9388	4.4700	0.0000	0.0000	3.4688	49.9218
17.050	592.000	0.550	0.000	51.542	17.0500	7.3971	3.8158	0.0000	0.5417	3.5813	51.5415
17.083	587.000	0.850	353.590	51.866	17.0830	7.3832	3.7794	0.0246	0.0385	3.6038	51.8657
17.120	583.000	0.800	342.720	52.048	17.1200	7.3708	3.7543	0.0244	0.0368	3.6165	52.0480
17.149	580.000	0.950	300.077	52.286	17.1490	7.3660	3.7330	0.0244	0.0292	3.6331	52.2864
17.249	752.500	1.550	0.000	52.286	17.2490	8.4657	4.8326	1.0997	0.0000	3.6331	52.2864
19.749	700.500	1.000	0.000	56.963	19.7490	8.4657	4.5077	0.0000	0.0000	3.9580	56.9627
23.320	607.000	2.150	0.000	65.857	23.3200	8.4657	3.8897	0.0000	0.0000	4.5760	65.8566
23.353	599.000	3.850	404.734	66.610	23.3530	8.4432	3.8149	0.0249	0.0474	4.6283	66.6099
23.386	593.500	3.750	316.382	66.994	23.3860	8.4363	3.7812	0.0248	0.0317	4.6550	66.9943
23.420	588.500	3.700	283.216	67.428	23.4200	8.4352	3.7501	0.0248	0.0258	4.6852	67.4280
23.452	583.500	3.900	339.376	67.762	23.4520	8.4239	3.7155	0.0246	0.0359	4.7084	67.7624
23.636	750.000	5.150	0.000	67.762	23.6360	9.4627	4.7543	1.0388	0.0000	4.7084	67.7624
27.636	648.500	0.800	0.000	76.083	27.6360	9.4627	4.1761	0.0000	0.0000	5.2865	76.0828
27.703	601.500	0.600	0.000	74.878	27.7030	9.0792	3.8763	0.0000	0.3835	5.2029	74.8783
27.736	598.500	0.650	300.355	75.086	27.7360	9.0736	3.8563	0.0240	0.0296	5.2173	75.0862
27.770	593.000	0.600	353.449	75.362	27.7700	9.0580	3.8215	0.0238	0.0393	5.2365	75.3622
27.803	588.500	0.600	318.889	75.637	27.8030	9.0481	3.7925	0.0235	0.0334	5.2556	75.6372
28.000	842.000	2.000	0.000	75.637	28.0000	10.6541	5.3986	1.6060	0.0000	5.2556	75.6372
32.390	751.500	0.900	0.000	83.710	32.3900	10.6541	4.8377	0.0000	0.0000	5.8165	83.7097
32.620	845.500	1.900	0.000	83.710	32.6200	11.2395	5.4230	0.5853	0.0000	5.8165	83.7097
43.870	706.000	0.500	0.000	96.253	43.8700	11.2395	4.5514	0.0000	0.0000	6.6881	96.2532
44.607	600.000	0.000	0.000	97.344	44.6070	10.6390	3.8751	0.0000	0.6005	6.7639	97.3443
44.643	590.500	0.800	360.000	98.168	44.6430	10.6238	3.8026	0.0245	0.0397	6.8211	98.1683
44.676	591.500	0.050	340.351	97.753	44.6760	10.6118	3.8195	0.0244	0.0364	6.7923	97.7527
44.710	587.000	-0.050	309.831	98.046	44.7100	10.6045	3.7919	0.0240	0.0313	6.8127	98.0462
44.743	583.500	0.000	333.800	98.204	44.7430	10.5922	3.7686	0.0236	0.0359	6.8236	98.2044

METHANE HYDRATE FORMATION RUN # 5
 DATE RUN STARTED: 11- 8-1987
 DATE RUN ENDED: 11-10-1987
 GRAMS OF H2O= 907.900
 GRAMS OF SAND= 920.200
 HEIGHT OF THE CORE= 29.84CM.
 ROOM TEMPERATURE= 21.0000DEG.C
 TEMP.OF GAS LEAVING WET TEST METER= 16.7000DEG.C
 BAROMETRIC PRESSURE= 744.600MM.HG
 VAP.PRESSURE OF WATER AT TWTN= 14.100MM.HG
 ICE TO SAND VOL.RATIO= 2.787
 ICE TO SAND MASS RATIO= 0.987
 PERCENTAGE VOIDS IN THE CORE= 44.388
 GMOL.METHANE FOR 100 PERCENT CONVERSION= 8.764191
 HYDRATE FORMATION RUN INPUT DATA

TIME (HR)	P1 (PSIA)	P3 (PSIA)	PL (PSIA)	PM (PSIA)	PR (PSIA)	T1RTD (DEG.C)	T2RTD (DEG.C)	FIREAD	WVTH (LIT)
0.00	634.00	632.00	629.00	630.00	633.00	-1.90	-1.10	0.00	0.00
0.15	614.00	614.00	620.00	611.00	613.00	-1.00	-0.50	0.00	1.89
0.18	580.00	580.00	582.00	574.00	576.00	-0.80	-0.50	20.40	3.55
0.22	560.00	560.00	565.00	550.00	560.00	-0.80	-0.30	19.70	4.76
0.25	546.00	544.00	550.00	542.00	544.00	-0.90	-0.30	18.60	5.47
0.28	532.00	530.00	537.00	540.00	531.00	-0.90	-0.10	18.40	6.25
0.40	878.00	877.00	885.00	858.00	877.00	-0.90	-0.30	0.00	0.00
1.32	654.00	653.00	582.00	564.00	614.00	-0.80	0.00	0.00	6.25
2.40	594.00	583.00	654.00	582.00	564.00	-0.70	0.10	19.70	8.46
2.43	582.00	581.00	654.00	582.00	564.00	-0.70	0.00	20.00	9.43
2.47	571.00	571.00	654.00	582.00	564.00	-0.70	0.10	18.60	10.23
2.50	564.00	563.00	654.00	582.00	564.00	-0.70	0.20	18.70	11.12
2.72	841.00	840.00	770.00	581.00	563.00	-0.80	-0.10	0.00	0.00
4.71	706.00	705.00	693.00	569.00	563.00	-0.60	0.30	0.00	11.12
4.79	610.00	609.00	679.00	569.00	563.00	-0.60	0.10	0.00	29.00
4.82	602.00	602.00	657.00	569.00	563.00	-0.60	0.20	20.60	30.50
4.85	593.00	593.00	644.00	568.00	563.00	-0.50	0.20	20.10	31.49
4.89	588.00	587.00	642.00	569.00	563.00	-0.50	0.20	19.30	32.51
4.92	583.00	583.00	640.00	569.00	563.00	-0.60	0.10	19.50	33.38
3.22	868.00	859.00	827.00	568.00	563.00	-0.70	0.20	0.00	0.00
11.97	617.00	615.00	599.00	565.00	562.00	-0.60	0.40	0.00	0.00
13.22	590.00	590.00	564.00	565.00	562.00	-0.60	0.40	0.00	33.38
13.25	582.00	582.00	564.00	565.00	562.00	-0.60	0.50	19.70	34.80
13.29	576.00	576.00	560.00	565.00	562.00	-0.60	0.70	19.70	35.06
13.39	571.00	570.00	557.00	565.00	562.00	-0.50	0.70	19.60	36.46
13.35	567.00	567.00	552.00	565.00	562.00	-0.40	0.70	19.40	37.31
11.55	840.00	839.00	789.00	565.00	562.00	-0.70	-0.40	0.00	0.00
16.65	792.00	790.00	735.00	565.00	562.00	-0.80	0.50	0.00	0.00
19.40	742.00	740.00	670.00	563.00	561.00	-0.60	0.70	0.00	0.00
26.63	649.00	648.00	547.00	563.00	561.00	-0.60	0.80	0.00	37.31
26.79	607.00	606.00	544.00	563.00	561.00	-0.60	0.80	0.00	42.15
26.82	604.00	603.00	537.00	563.00	561.00	-0.50	0.90	19.50	42.91
26.85	598.00	598.00	534.00	563.00	561.00	-0.70	0.90	20.30	43.72
26.89	593.00	592.00	532.00	563.00	561.00	-0.50	0.90	19.50	44.54
26.92	589.00	588.00	529.00	563.00	561.00	-0.50	0.90	19.40	45.30
27.42	857.00	857.00	737.00	563.00	859.00	-0.70	1.00	0.00	0.00
37.17	767.00	766.00	609.00	763.00	769.00	-0.60	0.70	0.00	0.00
40.17	715.00	685.00	563.00	561.00	713.00	-0.70	-0.50	0.00	0.00
47.07	654.00	654.00	525.00	647.00	653.00	-0.70	0.20	0.00	45.30
47.14	602.00	602.00	525.00	608.00	610.00	-0.70	0.10	0.00	50.35
47.17	598.00	597.00	525.00	598.00	601.00	-0.70	0.30	19.80	51.66
47.23	589.00	588.00	525.00	589.00	593.00	-0.60	0.30	19.60	52.71
47.24	583.00	582.00	525.00	585.00	589.00	-0.70	0.40	19.60	53.59
47.27	579.00	578.00	525.00	579.00	584.00	-0.70	0.30	19.50	54.36

RESULTS OF HYDRATE RUN

TIME (HR)	PBAR (PSIA)	TBAR (DEG.C)	QBAR (CC/MIN)	CONV (%)	TIME	GMLO	GMOLG	GMOLIN	GMLOUT	GMOLR	CONV
0.000	633.000	-1.000	0.000	0.000	0.0000	3.5603	3.5603	0.0000	0.0000	0.0000	0.0000
0.150	614.000	-0.250	0.000	0.416	0.1503	3.4804	3.4440	0.0000	0.0799	0.0365	0.4161
0.183	580.000	-0.150	535.276	2.095	0.1833	3.4356	3.2521	0.0254	0.0702	0.1836	2.0947
0.216	560.000	-0.050	423.837	3.083	0.2163	3.4090	3.1388	0.0245	0.0511	0.2702	3.0835
0.249	545.000	-0.100	297.770	3.958	0.2493	3.4021	3.0552	0.0231	0.0300	0.3469	3.9580
0.282	531.000	0.000	312.952	4.751	0.2823	3.3921	2.9757	0.0229	0.0330	0.4164	4.7510
0.399	877.500	-0.100	0.000	4.751	0.3990	5.3356	4.9192	1.9436	0.0000	0.4164	4.7510
1.316	653.500	0.100	0.000	19.110	1.3160	5.3356	3.6608	0.0000	0.0000	1.6748	19.1096
2.399	588.500	0.200	660.637	22.492	2.3990	5.2667	3.2955	0.0245	0.0934	1.9712	22.4918
2.432	581.500	0.150	369.096	22.748	2.4320	5.2506	3.2569	0.0249	0.0410	1.9937	22.7484
2.465	571.000	0.200	319.082	23.304	2.4650	5.2399	3.1975	0.0231	0.0338	2.0424	23.3043
2.498	563.500	0.250	341.091	23.626	2.4980	5.2256	3.1549	0.0233	0.0376	2.0707	23.6263
2.715	840.500	0.050	0.000	23.626	2.7150	6.7799	4.7092	1.5543	0.0000	2.0707	23.6263
4.715	705.500	0.350	0.000	32.306	4.7150	6.7799	3.9485	0.0000	0.0000	2.8314	32.3062
4.788	609.500	0.250	0.000	29.800	4.7880	6.0241	3.4125	0.0000	0.7557	2.6117	29.7995
4.821	602.000	0.300	498.782	29.855	4.8210	5.9864	3.3699	0.0256	0.0634	2.6165	29.8547
4.854	593.000	0.350	374.529	30.244	4.8540	5.9695	3.3189	0.0250	0.0418	2.6507	30.2443
4.887	587.500	0.350	376.057	30.378	4.8870	5.9504	3.2881	0.0240	0.0431	2.6624	30.3776
4.920	583.000	0.250	341.931	30.509	4.9200	5.9379	3.2641	0.0243	0.0368	2.6738	30.5086
5.220	863.500	0.250	0.000	30.509	5.2200	7.5084	4.8345	1.5705	0.0000	2.6738	30.5086
11.970	616.000	0.400	0.000	46.341	11.9700	7.5084	3.4470	0.0000	0.0000	4.0614	46.3411
13.220	590.000	0.400	0.000	48.001	13.2200	7.5084	3.3015	0.0000	0.0000	4.2069	48.0011
13.253	582.000	0.450	473.565	48.114	13.2530	7.4729	3.2561	0.0245	0.0600	4.2168	48.1135
13.286	576.000	0.550	198.877	48.664	13.2860	7.4864	3.2214	0.0245	0.0110	4.2650	48.6642
13.391	570.500	0.600	468.132	48.625	13.3910	7.4516	3.1900	0.0244	0.0592	4.2616	48.6249
13.352	567.000	0.650	336.498	48.720	13.3520	7.4398	3.1699	0.0241	0.0359	4.2699	48.7203
13.552	839.500	-0.050	0.000	48.720	13.5520	8.9753	4.7053	1.5355	0.0000	4.2699	48.7203
16.652	791.000	0.350	0.000	51.896	16.6520	8.9753	4.4270	0.0000	0.0000	4.5483	51.8960
19.402	741.000	0.550	0.000	55.123	19.4020	8.9753	4.1442	0.0000	0.0000	4.8311	55.1235
26.625	648.500	0.600	0.000	61.034	26.6250	8.9753	3.6262	0.0000	0.0000	5.3491	61.0337
26.785	606.500	0.600	0.000	61.379	26.7850	8.7707	3.3913	0.0000	0.2046	5.3794	61.3792
26.820	603.500	0.700	315.883	61.495	26.8200	8.7628	3.3733	0.0243	0.0321	5.3895	61.4949
26.853	598.000	0.600	333.299	61.729	26.8530	8.7539	3.3438	0.0253	0.0342	5.4101	61.7293
26.887	592.500	0.700	330.091	61.975	26.8870	8.7435	3.3118	0.0243	0.0347	5.4316	61.9753
26.920	588.500	0.700	315.186	62.139	26.9200	8.7355	3.2895	0.0241	0.0321	5.4460	62.1393
27.420	857.000	0.650	0.000	62.139	27.4200	10.2372	4.7911	1.5017	0.0000	5.4460	62.1393
37.170	766.500	0.550	0.000	67.894	37.1700	10.2372	4.2868	0.0000	0.0000	5.9504	67.8944
40.170	700.000	-0.100	0.000	72.032	40.1700	10.2372	3.9242	0.0000	0.0000	6.3130	72.0316
47.070	654.000	0.250	0.000	75.027	47.0700	10.2372	3.6616	0.0000	0.0000	6.5756	75.0275
47.140	602.000	0.200	0.000	75.907	47.1400	10.0237	3.3711	0.0000	0.2134	6.6526	75.9069
47.171	597.500	0.300	448.214	75.858	47.1730	9.9930	3.3447	0.0246	0.0554	6.6483	75.8577
47.230	588.500	0.350	385.252	76.211	47.2300	9.9730	3.2937	0.0244	0.0444	6.6793	76.2112
47.240	582.500	0.350	344.996	76.448	47.2400	9.9602	3.2601	0.0244	0.0372	6.7001	76.4482
47.273	578.500	0.300	318.251	76.602	47.2730	9.9519	3.2383	0.0243	0.0325	6.7136	76.6023