OVERVIEW ON HYDRATE CORING, HANDLING AND ANALYSIS

TOPICAL REPORT – FINAL

Reporting Period: July 2, 2002 through June 30, 2003

Editors: Dr. Jon Burger, Dr. Deepak Gupta, Patrick Jacobs and John Shillinglaw

Issued: AUGUST 2006

Department of Energy Award No. DE-FC26-02NT41327

Intertek Westport Technology Center
6700 Portwest Drive
Houston, Texas 77024
(713) 479-8400
(713) 864-9357 (Fax)
www.westport1.com

Prepared for the U.S. Department of Energy

This manual was prepared with the support of the U.S. Department of Energy under Award No. DE-PS26-NT41327. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the DOE. Westport Technology Center International makes no representations or warranties, either expressed or implied, and specifically provides the results of this report "as is", based on the information from the searched literature.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trade mark, manufacturer, or otherwise does not necessarily constitute its endorsement, recommendation or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily reflect those of the United States Government or any agency thereof.

ABSTRACT

Gas hydrates are crystalline, ice-like compounds of gas and water molecules that are formed under certain thermodynamic conditions. Hydrate deposits occur naturally within ocean sediments just below the sea floor at temperatures and pressures existing below about 500 meters water depth. Gas hydrate is also stable in conjunction with the permafrost in the Arctic. Most marine gas hydrate is formed of microbially generated gas. It binds huge amounts of methane into the sediments. Worldwide, gas hydrate is estimated to hold about 1016 kg of organic carbon in the form of methane (Kvenvolden et al., 1993). Gas hydrate is one of the fossil fuel resources that is yet untapped, but may play a major role in meeting the energy challenge of this century.

In June 2002, Westport Technology Center was requested by the Department of Energy (DOE) to prepare a “Best Practices Manual on Gas Hydrate Coring, Handling and Analysis” under Award No. DE-FC26-02NT41327. The scope of the task was specifically targeted for coring sediments with hydrates in Alaska, the Gulf of Mexico (GOM) and from the present Ocean Drilling Program (ODP) drillship. The specific subjects under this scope were defined in 3 stages as follows: Stage 1: Collect information on coring sediments with hydrates, core handling, core preservation, sample transportation, analysis of the core, and long term preservation. Stage 2: Provide copies of the first draft to a list of experts and stakeholders designated by DOE. Stage 3: Produce a second draft of the manual with benefit of input from external review for delivery.

The manual provides an overview of existing information available in the published literature and reports on coring, analysis, preservation and transport of gas hydrates for laboratory analysis as of June 2003. The manual was delivered as draft version 3 to the DOE Project Manager for distribution in July 2003. This Final Report is provided for records purposes.

TABLE OF CONTENTS

LIST OF TABLES

Tables ***Page***

LIST OF FIGURES

Figures **Page**

Executive Summary

Westport Technology Center was requested by the Department of Energy (DOE) to prepare a “Best Practices Manual on Gas Hydrate Coring, Handling and Analysis” under Award No. DE-FC26-02NT41327. The scope of the task was specifically targeted for coring sediments with hydrates in Alaska, the Gulf of Mexico (GOM) and from the present Ocean Drilling Program (ODP) drillship. The specific subjects under this scope were defined in 3 stages as follows:

Stage 1:

- Coring sediments with hydrates
- Core handling at the rigsite
- Core preservation at the rigsite
- Transportation of the core
- Analysis of the core
- Long term preservation of the core

Stage 2:

- Provide copies of the first draft to a list of experts and stakeholders designated by DOE. It is intended that they would review and provide further input, and possibly provide additional best practices content and references, within a 1-2 week period.

Stage 3:

- Produce a second draft of the manual with benefit of input from external review for delivery.

In the manual we provided an overview of existing information available in the published literature and reports on coring, analysis, preservation and transport of gas hydrates for laboratory analysis. The manual contains method of coring sediments containing gas hydrates, the equipment available for coring and their relative performances, handling and analysis of the cores at rigsite and their preservation for transport to the destined laboratory for further analysis and preservation. A brief description of natural gas hydrates and their characteristic in-situ are presented to acquaint the reader with different scenarios of gas hydrate formation and dissociation. The major sources of information are books, monographs, reports, workshops, and several other references contained therein, along with the recent published articles in journals and private communications (see, for example, Sloan (1998), Proceedings of JAPEX/JNOC/GSC Mallik 2L-38 by Dallimore et al (1999), Report of DE-FC26-01NT41329 by Rack (2001), Low Invasion Coring Manual by Bloys (2001), Westport Core Handling Manual, Proceedings of Yokohama Conference on Gas Hydrates (2002), ChevronTexaco JIP Workshop (2002), Westport/Maurer/Anadarko Workshop (2002), Texas A&M Pressure Coring Workshop(2003).

Methodologies and techniques related to acquiring the most representative natural gas hydrate samples, for example: (1) maintaining core at reservoir conditions after drilling or coring, (2) use of conventional and pressure-temperature coring equipment, (3) estimating gas hydrate pore saturation in the core, and (4) handling and transporting samples for laboratory analysis (from the rigsite to the laboratory) in an efficient and cost effective manner are very important. The latter is particularly important for unconsolidated cores acquired in the Gulf of Mexico.

To create models to predict behavior of gas hydrate 1) during exploration and production field operations, and 2) to understand their relationship with naturally destabilizing and formation events and processes, requires input properties determined from representative samples. Although producing high-quality input data is difficult and expensive, it is critical to understanding natural behavior.

The First Draft, Version 1, was provided to a list of experts and stakeholders designated by DOE in May 2003, with the intention that they would review and provide further input, and possibly provide additional best practices content and references. To this point we have received constructive and encouraging suggestions from a number of experts, via their presentations and personal discussions at Westport/Maurer/Anadarko Workshop (2002) and the ODP Pressure Coring Workshop (2003). We incorporated the majority of their suggestions in this version. The most recent experience of Leg 204 ODP expedition in the Pacific Ocean off the Oregon coast is also summarized briefly in Appendix B.

Draft Version 3 was issued to DOE for distribution in July 2003. This Final Report is provided for records purposes.

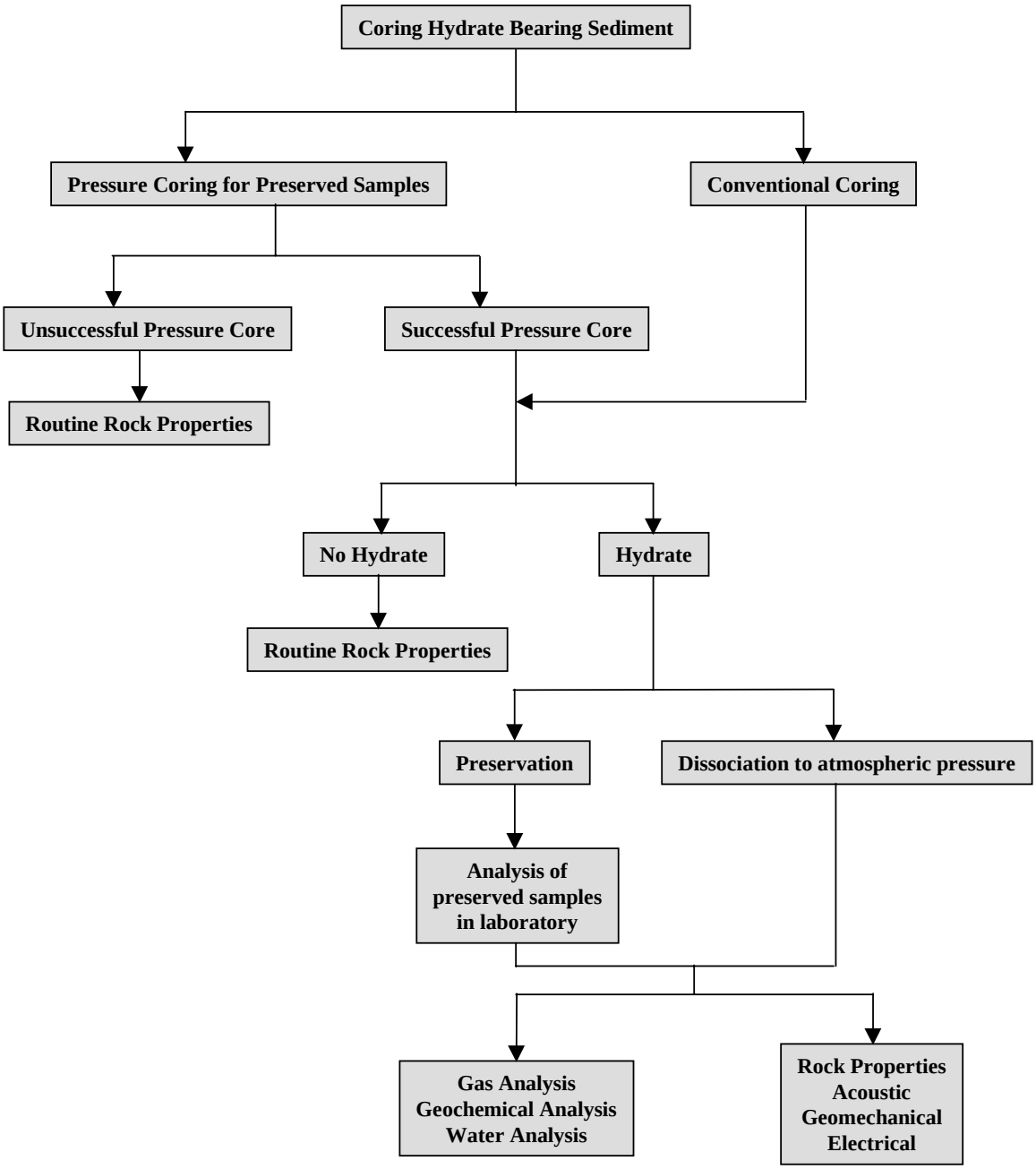
1.0 INTRODUCTION

Natural Gas hydrates are widespread in permafrost regions and beneath the sea within sediments of outer continental margins. Methane is the most commonly trapped gas molecule in natural hydrate. Estimates show that 1 m^3 of hydrates can liberate up to 164 m^3 of gas (assuming 90% cave occupancy at standard temperature and pressure). Gas hydrates are important to petroleum industries for: 1) use as an alternative source of energy, 2) oil and gas production, and 3) transportation and storage. However, gas hydrate formation is hazardous to drilling and production operations, as they pose several risks, such as plugging of pipelines, plugging of kill and choke lines, and blocking the drill string in deep and ultra-deep offshore drilling operations. In addition, hydrates may be responsible for greenhouse effects by liberating methane and carbon dioxide gases in to the atmosphere. Conversely, hydrates can be used for sequestration of greenhouse gases in the bottom of the ocean. Therefore, evaluation, remediation and prevention of the problems, safe drilling through gas hydrates, and production of hydrocarbons from gas hydrates, are currently active areas of research and development.

In the next section the scope of this work is defined. Section 3 provides a brief presentation on the general concept of gas hydrates and their characteristics and stability in sediments in particular, in the Gulf of Mexico (GOM) scenarios and Alaska permafrost region. Section 4 presents the details on coring equipment utilized in sediments with hydrates, and Section 5 discusses coring operations. Section 6 presents hydrate verification tests, core handling and processing at the rigsite. Section 7 presents how to analyze the core at the surface ensure that the core contains gas hydrate, as well as how to preserve the core at rigsite. Section 8 provides the method of core transportation and monitoring to the selected laboratory for analysis. Section 9 discusses various methods of analysis and characterization of the core, and the method of hydrate verification at the laboratory facility. Section 10 suggests long term core preservation method for any future analysis and characterization. Section 11 provides the summary of the work followed by some recommendations.

A brief summary of coring and analysis technology is presented in the following chart. It represents an overview of this manual.

Figure 1.1 A Flow Chart of Coring and Analysis Technology



2. SCOPE OF WORK

Development of gas hydrate drilling and characterization technologies requires closely monitored, and well-controlled drilling and extraction practices, for the safe production of hydrocarbons. Under the Department of Energy (DOE) gas hydrate program, Westport Technology Center was contracted to prepare a "*Best Practices Manual on Gas Hydrate Coring, Handling and Analysis*".

The scope of work was specifically targeted at coring sediments containing hydrates in Alaska, GOM and from the ODP drill ship. The specific subjects under the scope were:

- Coring of Sediments with Hydrates
- Core Handling at Rigsite
- Core Preservation at Rigsite
- Transportation of the Core
- Analysis of the Core
- Long Term Preservation of the Core

The First Draft, Version 1 was provided to a list of experts and stakeholders designated by DOE, with the intention that they would review and provide further input, and possibly provide additional best practices content and references. To this point, we have received constructive and encouraging suggestions from a number of experts via their presentations and personal discussions at Westport/ Maurer/ Anadarko Workshop (2002). After reviewing their available works, we have incorporated the majority of their suggestions in this version. However, their specific comments/inputs to improve upon the Draft Manual Version.1 are still awaited.

In this document, we first provide the general introduction of the gas hydrate formation and dissociation (with and without sediment), which is important for the understanding and analysis of coring through gas hydrates. The discussion of available coring technology and equipment is then presented. Whether the cores contain gas hydrates, and how to verify at wellsite, are the major questions to be answered. These are discussed in the light of currently available literature and experience by the gas hydrate drilling community. The preservation of the cores, preparation for transportation, and analysis at the destined laboratories are discussed in a greater detail. Finally, the preservation of the cores for the short and long term is discussed, and recommendations are made for drilling through gas hydrate in the GOM and Alaska. The most recent experience of Leg 204 ODP expedition in the Pacific Ocean (off the Oregon) coast, due to Rack and team (2002), is also summarized briefly in Appendix A.

3. GAS HYDRATES IN GENERAL

Natural gas hydrates are crystalline, nonstoichiometric, solid clathrate compounds. The crystalline compound is composed of hydrate forming gas molecules, such as methane, ethane, propane, butane, carbon dioxide, hydrogen sulfide and nitrogen, entrapped in a cage formed by surrounding hydrogen bonded water molecules. The gas hydrates formed by these gases can have structure sI (body centered cubic) and structure sII (diamond lattice). More complex systems, containing methane through pentane (C1-C5), may have structure sH, as well. Conditions of formation and dissociation of these gas hydrates depend on gas composition, aqueous phase composition, and presence of a liquid hydrocarbon phase, along with the suitable conditions of low temperature and high pressure. Gas hydrates of sII and sH are stable at higher temperatures and lower pressures than gas hydrate of sI. The unit cell of structure sI hydrates consists of 46 water molecules, and includes two small (5.2 Å) and six large (5.9 Å) cavities. For structure sII hydrates the unit cell consists of 136 water molecules and includes 16 small cavities and 8 large cavities. The large cavities of structure sII have a mean diameter of 6.6 Å. The small cavities of sI and sII are a pentagonal dodecahedron. The large cavity of structure sI is a tetrakaidecahedron and that of structure sII is a hexakaidecahedron. The molecular characteristics are important to identify the presence of gas hydrates during drilling operations. An excellent review on general characteristics and properties of gas hydrates can be found in several recent articles and monographs (see, for example, Kvenvolden, 1993; Kvenvolden et al, 1993; Max, 2000; Max and Lowrie, 1992, 1996; Lowrie et al, 1997; Howell, 1993; Fleischer et al, 2001; Sloan, 1998, 2000; Collett et al, 2000; Shukla et al, 2000; Proceedings on Gas Hydrates, Yokohama May 19-23, 2002; Dallimore et al, 1999; Holder, 2000; OTC Proceedings, 2002 (and references therein), and personal communications).

Drilling and production of gas hydrates in deep water conditions, such as Gulf of Mexico (GOM), are challenging tasks because gas generated by hydrate dissociation may be an explosion hazard for drilling rigs, production platforms and pipelines. The conditions of wellbore stability and seafloor instability are other important factors to take into consideration. Vigorous efforts are being made by both industry and academia to understand the gas hydrate drilling operations and production of methane gas safely from GOM, supported by U.S. Department of Energy and oil and gas companies (see, for example, the websites of ChevronTexaco JIP, 2002 and DOE). A list of websites is included in Appendix C.

Figure 3.1 shows the gas hydrate dissociation lines for methane (internal Westport). The hydrate dissociation line for a typical GOM gas mixture (Green Canyon) is given in Figure 3.2 (internal Westport). The hydrate dissociation curves in these figures represent the hydrate equilibrium conditions. As indicated in Figures 3.1 and 3.2, there is no gas hydrate formation to the right hand side of the equilibrium line (no hydrate), while there is gas hydrate formation to the left-hand side of the equilibrium line (hydrate). Figure 3.3 shows the schematic representation of the hydrate stability region of methane gas as a function of temperature and depth (after Lowrie and Lerche 2002).

Generally, methane gas becomes hydrated at water depths of about 400 m. However, methane with a 10% mixture of ethane can hydrate as shallow as 100 m (Baker, 1974). With increased water depth the thickness of the hydrate stability zone increases and in sufficient water depth the hydrate stability zone can be up to a kilometer thick. Such a behavior can be seen in Figures 3.1 and 3.4. Figure 3.4 shows the quantitative hydrate phase behavior for methane and Green Canyon gases along with a sea water temperature profile.

Since nitrogen is sometimes used to preserve the gas hydrate for transportation and laboratory analysis, Figure 3.5 shows gas hydrate dissociation lines for mixtures of nitrogen and methane gases. Nitrogen may be utilized as a pressurizing gas for the transportation of the sediment containing hydrate. However, contamination of gas hydrate by nitrogen gas may occur, although maintaining temperature and pressure conditions that are stable for gas hydrates can reduce the contamination effects.

In recent years, some important observations have been made on the stability of gas hydrates in sediments. Outcropping thermogenic gas hydrate at Green Canyon Block 185 (~540 m water depth) is only transiently stable because of episodic warm cored eddy currents causing natural fluctuations in the temperature of seawater. However, the observed increases in seafloor water temperature are generally of short duration and, hence, the transient decomposition of gas hydrates may be limited to the upper 2 m of sediments (Milkov et al, 2000). Because deeper gas hydrate is insulated from transient increases of seawater temperature, the deeper gas hydrate is more stable.

While drilling, the general chemosynthetic concern is obvious. Chemosynthetic communities are composed of bacterial mats and larger fauna, such as tubeworms, mussels, clams, and associated organisms. Where abundant on the seafloor, free gas and gas hydrate impact microbially mediated processes in chemosynthetic communities that depend on methane and hydrogen sulfide (Sassen et al, 1999). The association between outcrops of gas hydrate and complex chemosynthetic communities affects exploration and exploitation in the GOM because the chemosynthetic communities need to be avoided.

Figure 3.1 Hydrate Dissociation Line for Methane

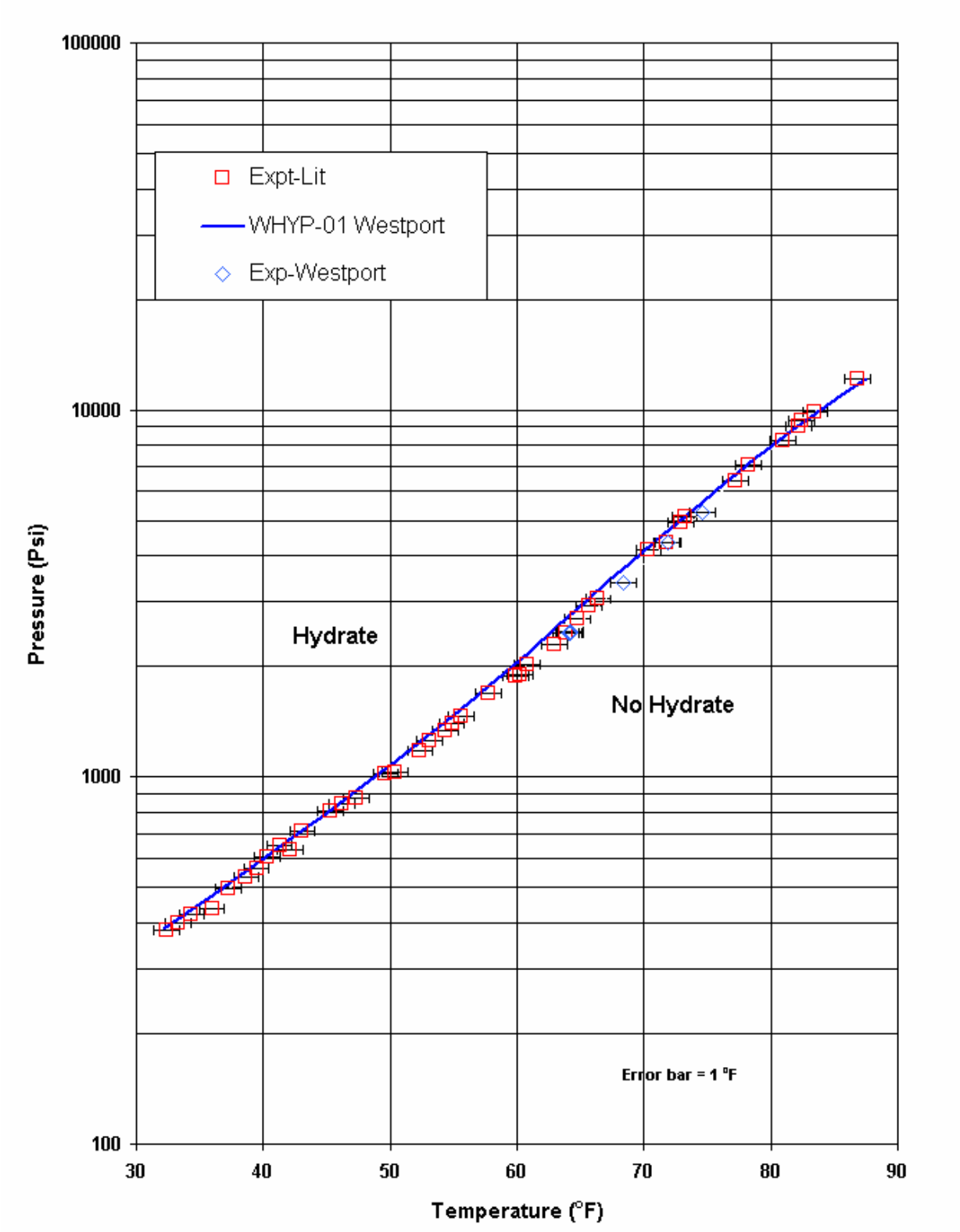


Figure 3.2 Gas Hydrate Dissociation Line for Green Canyon Gas

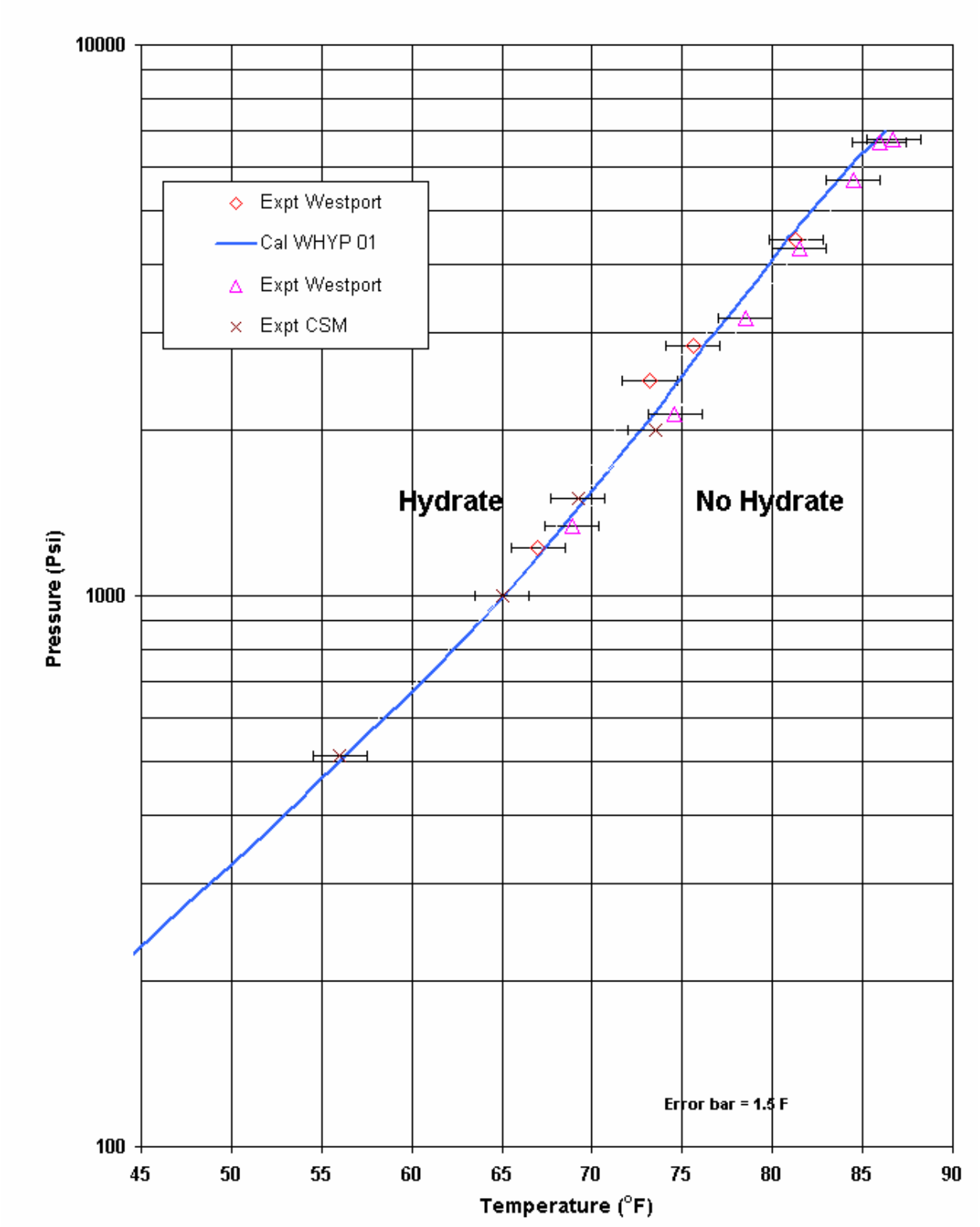


Figure 3.3 Schematic Illustration of Methane-Hydrate Stability Zone for Offshore

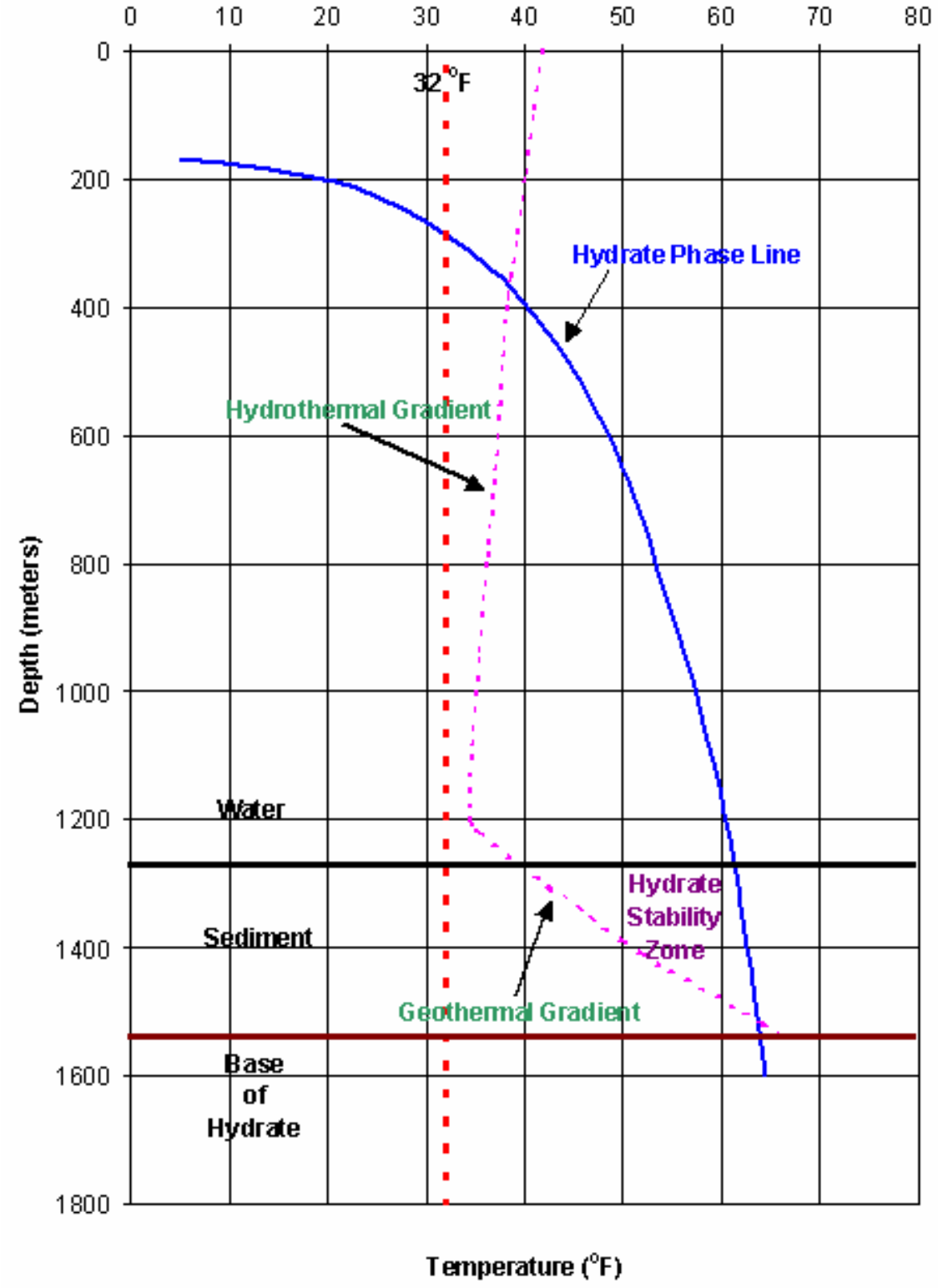


Figure 3.4 Schematic Illustration of Methane-Hydrate Stability Zone for Offshore

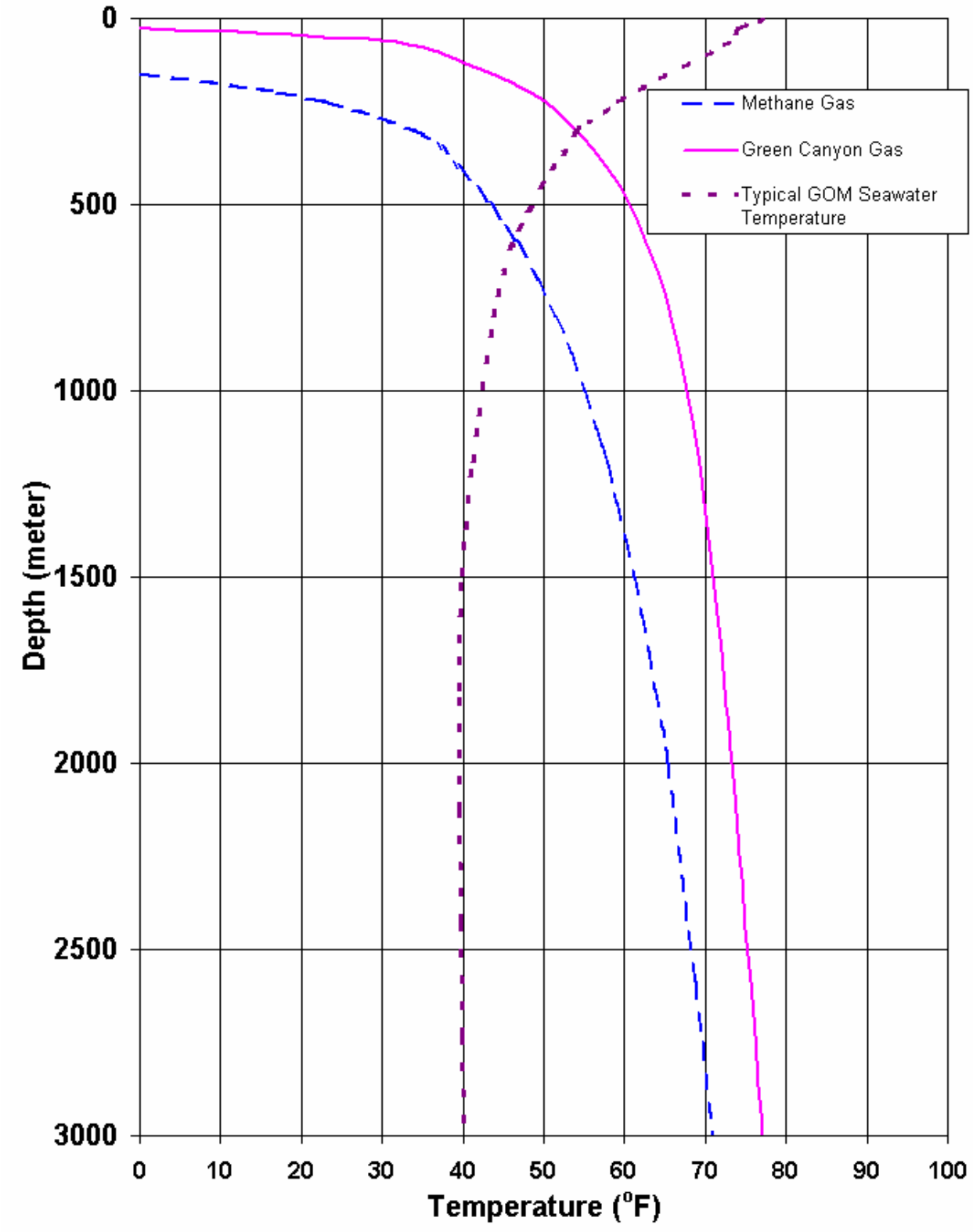


Figure 3.5 Schematic Illustration of Methane-Hydrate Stability Zone for Artic

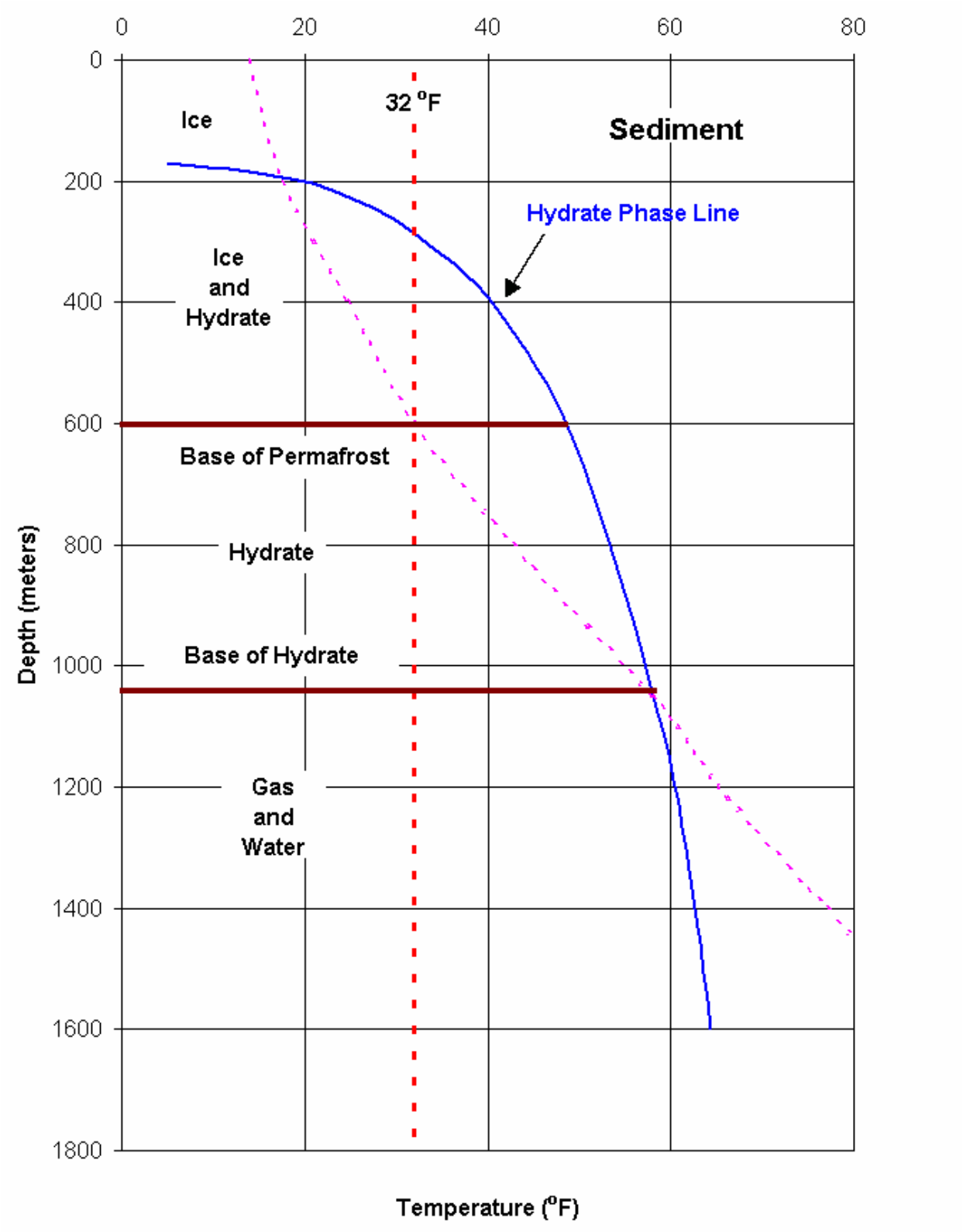


Figure 3.6 Gas Hydrate Dissociation Line for Mixed System of N2/C1 (Predicted)

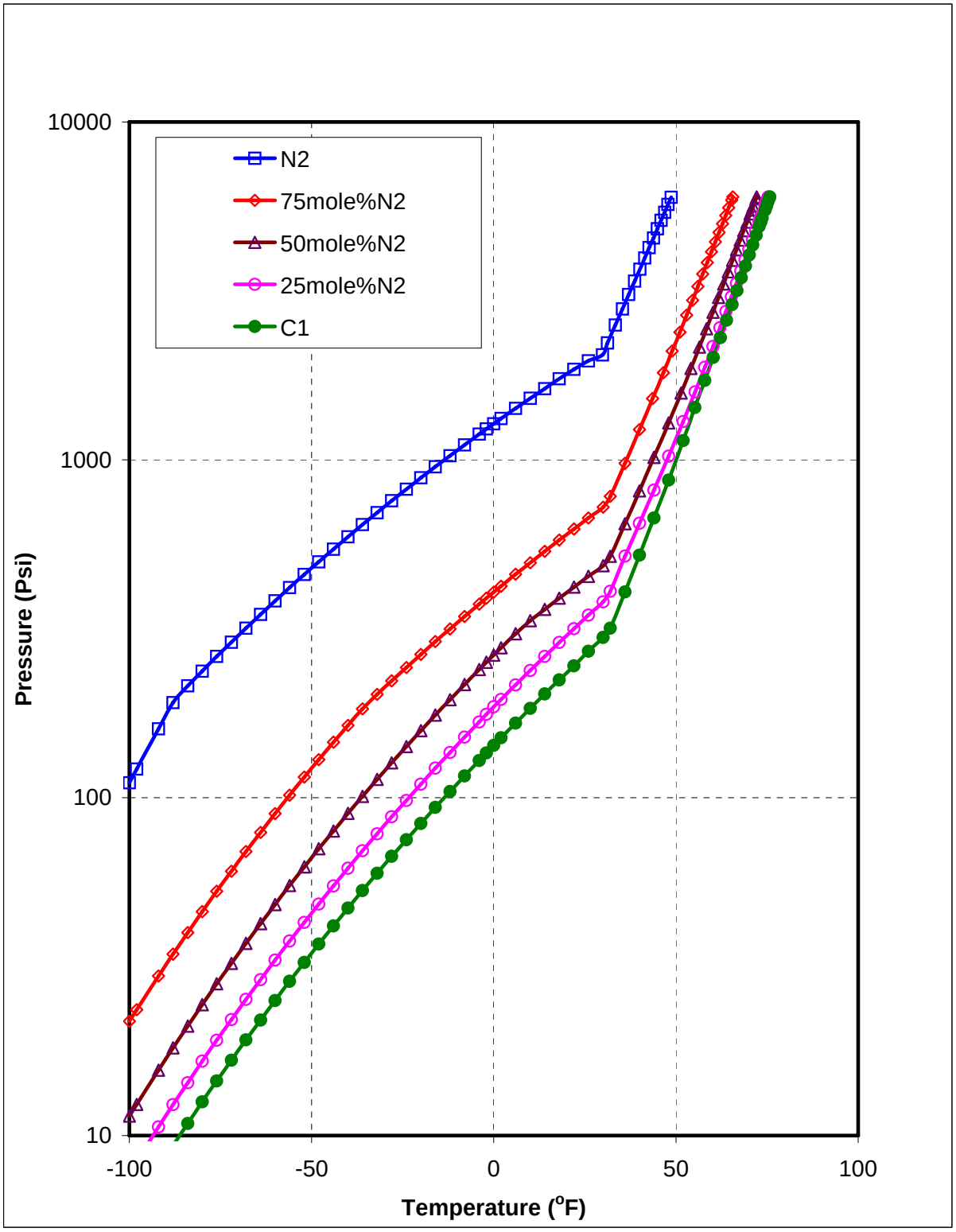


Table 3.1 presents a comparative study on some important physical properties of both a typical methane gas hydrate and ice, in order to provide a guideline for understanding the methane dominated gas hydrate reservoirs.

Table 3.1 Physical Properties of Methane Gas Hydrates and Ice (Davidson, 1983; Prensky, 1995; Sloan, 1998)*

Property	**Ice**	**Hydrate**
Density (g/cm^3)	0.916	0.912
Dielectric Constant at 273K (32 ^{o}F)	94	58
Thermal Conductivity @ 263K (14 ^{o}F) (W/m-K)	2.23	0.49
Adiabatic Bulk Compressibility @ 273K (32 ^{o}F) (10^{-11} Pa)	12	14
Isothermal Young's Modulus @ 268K (29 ^{o}F) (10^9 Pa)	9.5	8.4
Bulk Modulus @ 272K (30 ^{o}F)	8.8	5.6
Shear Modulus @ 272K (30 ^{o}F)	3.9	2.4
Poisson's Ratio	0.33	0.33
Velocity Ratio Vp/Vs @ 272K (30 ^{o}F)	1.88	1.95
Speed of Longitudinal Sound @ 273K (32 ^{o}F)		
Velocity (km/s)	3.8	3.3
Transit time (μs/ft)	80	92
NMR Rigid Lattice 2nd Moment of H2O protons (G^2)	32	33
Water Molecule Reorientation Time @ 273K (32 ^{o}F) (μs)	21	10
Diffusion Jump Time of Water Molecule @ 273K (32 ^{o}F) (μs)	2.7	> 200

* Properties of gas hydrate in sediments under various scenarios are discussed in Section 9.

3.1 Sediment Fabric

Oceanic hydrates have been recovered in some of the thousands of Ocean Drilling Program (ODP) boreholes from which over 250 km of cores have been taken (Rack, 2001 and references therein). The majority of the hydrates dissociated when brought on deck, although a few samples were preserved for further analysis. Hydrates in the cores were found mostly as dispersed grains or thin laminate. Massive pieces of hydrates, larger than 10 cm thick, have also been found. However, in many cases the inferred presence of hydrates depends on bottom simulating reflectors (BSR) or chlorinity changes in the pore water. The understanding of oceanic gas hydrates is still a challenging problem because of the poor quality of measurements in soft sediments (cores, samples and logs), and the lack of calibration of seismic against the known oceanic hydrate systems. On land, in the Malick 2L-38 well drilled in the Mackenzie Delta, sub-permafrost hydrates were located in coarser grained sand deposits, not in interbedded silts (Dallimore et al, 1999). Coarse-grained hydrate bearing reservoirs in the MacKenzie Delta are significantly different from the finer-grained offshore sediments.

3.2 Historical Background of Producing Gas from Gas Hydrates

The first production of gas from a hydrate layer occurred in the Siberian Messoyakha gas field in 1968, when dissociation of gas hydrates resulted from a pressure decrease in the free gas zone (Collett et al, 2000). The method of depressurization for producing gas from gas hydrates could be suitable for those fields, as well where the free gas is associated with hydrate accumulation. This effort was followed by the study of gas hydrates accumulation in Prudhoe Bay in Alaska, where gas hydrates were recovered in pressurized core barrels (Collett, 1993). The thickness of the zone of gas hydrate stability for this area was calculated from the temperature and pressure gradients in the region, and the hydrates were found stable between 210 m and 950 m. 445 additional wells in the North Slope were examined using well-log data. An estimated 50 wells contained gas hydrates in six laterally continuous sandstones at the east end of Kuparuk River, and west end of the Prudhoe Bay production units. Hydrate cores were also recovered. The investigations of gas hydrates associated with the conventional hydrocarbon accumulations suggested that borehole-logging tools (such as single and multiple types of logs, acoustic and resistivity logs) could identify hydrate zones in the Arctic.

Similar to hydrate wells in the U.S. Arctic, the Mallik Well 2L-38 in the Mackenzie Delta was drilled and cased through the permafrost, reaching a depth of 640 m. The permafrost zone was logged with several Schlumberger wireline tools, such as induction imager tool, dipole shear sonic imager and Platform Express tool strings, etc. Below the permafrost the well was drilled and cored to 1150 m. This subpermafrost region was logged with the same tools and FMI fullbore formation microlmager tool. The hydrate bearing region extended from 897.5 m to 1109.5 m. A mud chiller was employed to increase the hydrate stability. The presence of gas hydrate was confirmed in an interval more than 200 m using downhole electrical resistivity and acoustic velocity logs. Deep

electrical resistivity values range from 10 Ohm-m to 100 Ohm-m. Compressional wave speed (Vp) ranges from 2.5 to 3.6 km/s and shear velocity (Vs) ranges from 1.1 to 2 km/s. The low value of Vp/Vs at the base of hydrate zone indicated a thin layer of free gas. The measurements on the core agree well with log-derived values of pore-water resistivity, porosity, and bulk and grain densities. Core and wellbore images indicated that the reservoir was high quality sandstone, with hydrates filling the pores. The range of porosity was 20% to 40%. No hydrates were found in the neighboring shale layers. Gas hydrate saturation was computed with more than 90% presence of hydrate saturation in some zones. The volume of hydrates determined from log and core data was ~ 3-4 x 10^9 m^3 of gas in a 1-km^2 area surrounding the well.

In order to find hydrates in the marine environment, the distribution of hydrates in sediments and the mechanical properties of hydrate bearing formations, must be properly understood. In such a case, hydrates could occur as individual particles disseminated in the sedimentary section, intergranular cement, nodules, laminae, veins and massive layers. Generally, the hydrate bearing sections vary in thickness from a few centimeters to 30 m. The occurrence of a BSR in seismic reflection results is the most important indicator of hydrates in marine sediments. However, hydrates can exist without a BSR if there is no underlying free gas, or the hydrates do not appreciably stiffen the sediment matrix (Yuan and Edwards, 2000). Depth of BSR below sea bottom depends on the temperature and pressure required for hydrate stability.

The experience gained from the 2L-38 Mallik well was utilized to drill through gas hydrates in the Nankai trough, offshore Japan. Several areas were identified by BSR as potential hydrate reservoirs. In this case, an exploratory well was drilled in 945 m depth of water (Uchida et al, 2000). Two pilot holes and a main hole were drilled to 1600 m and 3300 m, respectively. Cores were acquired and measurements were made, including chlorine anomalies, logging-while-drilling density, neutron, dual induction and bit resistivity, openhole wireline dipole shear and compressional velocities, laterolog and nuclear magnetic resonance. The maximum gas hydrate saturation was estimated to be 80% of total porosity in the reservoir sandstone.

Offshore BSRs have been mapped at depths below the seafloor ranging from 100 m to 500 m such as in regions of the Offshore Blake Ridge. Their shape tracks the shape of the sea bottom. In fact, the velocity of sound in pure hydrate is almost the same as that of ice and the exact value depends on hydrate chemistry. Acoustic velocity in a hydrate-cemented layer is higher than in fluid filled sediments. Consequently, the contact between a hydrate rich layer and a gas filled layer acts as a prominent seismic reflector, which occurs at the base of the hydrate zone (known as BSR). There is no unique consensus on the occurrence of BSR in the GOM.

To date, a universally agreed upon systematic method for drilling, coring and preserving the gas hydrate regions in the GOM and other regions, does not exist. Transporting and preserving the hydrate cores for further analysis and characterization also needs further development. The purpose of the hydrate coring manual is to supply the gas hydrate community with a systematic method to core in the hydrate bearing reservoirs related

with the GOM and Alaska, and recover, transport and preserve the cores for detailed analysis and testing in the laboratory, under well-controlled conditions.

3.3 Special Considerations Due to Operating Conditions

Coring for preserved hydrate samples is unlike conventional coring. First, temperatures are much lower than normal oilfield conditions, with operating temperatures of ~ 40 ^{o}F. Second, in many cases, the hydrate will be gone before the sample can be retrieved. This causes a re-evaluation of techniques. Conventional coring with all equipment attached to the drillstring and retrieved by removing the entire drillstring, will (in most cases) lead to destruction of the hydrates within the core sample, thus negating the value of the operation. The value of a fast withdrawal of a hydrate sample from the subsurface is paramount. Therefore, wireline-coring tools are recommended. Third, in order to accomplish the same goal, there are many different techniques to use that are somewhat environment dependent.

The disparity in the temperature profiles allows the Arctic coring procedure to vastly differ from the procedures employed in the Gulf of Mexico, where surface temperatures are much higher. Figure 3.4 illustrates the hydrate stability curve for methane hydrate and Green Canyon gas hydrate. Also shown is the average water temperature versus depth, in the Gulf of Mexico. Whether a partially dissociated hydrate can be restored to original conditions, or by what technique, is not properly understood at present. In the following sections, coring equipment will be reviewed along with the objectives of the operation and operating conditions.

Preserved hydrate samples are required for testing. Fully preserved hydrate means formation pressure, formation temperature, and original hydrate compositions have been maintained throughout the process. Conventional freezing techniques may not be sufficient to preserve the gas hydrate samples.

3.4 Unconsolidated Sediments

Unconsolidated sediments are commonly found in the Gulf of Mexico, even as deep as 20,000 feet. Coring unconsolidated material presents many challenges. Conventional core catchers are not efficient. Loss of material due to poor bit or catcher design is common, and conventional handling can damage the core integrity. Oilfield coring companies have spent extraordinary efforts to better core unconsolidated material. Core recoveries of greater than 90% are now common in areas such as the Gulf of Mexico, West Africa, Venezuela, California, and Canada, all areas producing conventional hydrocarbons from highly unconsolidated sediment. Procedures for handling these sediments from the coring operation to the laboratory have been under development for several years.

In a recent laboratory work, Turner and Sloan (2001) demonstrated that unconsolidated sediments have free expansion, and capillaries are dominated by grain spaces. In a ceramic core of methane gas hydrate with infinite average pore size, the change in

equilibrium temperature (ΔTeq), from inside core, to outside core was investigated. The authors concluded that the consolidated data with model tetrahydrofuran (THF) showed some ΔTeq, while consolidated large pore methane data showed no ΔTeq. Further investigations in a laboratory setup are in progress to understand the behavior of gas hydrates for consolidated and unconsolidated hydrate cores.

4. CORING EQUIPMENT

4.1 Hydrate Coring

The techniques for coring hydrate-bearing sediments are mainly based on pressure wireline coring and conventional wireline coring. However, the Mallick 2L-38 well drilled in the Mackenzie Delta in 1998, utilized a conventional, drillpipe-conveyed system to recover gas hydrate containing core. Currently, four pressure coring systems exist which can be used for hydrate coring operations. The extensively used Ocean Drilling Program's (ODP) Pressure Coring System (PCS) is an upgraded and modified version based on the original design by Jim Aumann. Jim Aumann and Associates developed a new design with a Japanese consortium of JAPEX, JNOC, etc., called the Pressure Temperature Coring System (PTCS). The HYACE (HYdrate Autoclave Coring Equipment) Rotary Corer (HRC), and FUGRO Pressure Corer (FPC), both developed through the European Union research project, are two other systems. Table 4.1 summarizes the specifications for wireline pressure coring systems using a rotary bit. Table 4.2 summarizes the existing equipment for wireline pressure coring using a piston corer. Table 4.3 summarizes the current drill pipe conveyed pressure coring systems. Table 4.4 summarizes the existing conventional (non-pressurized) wireline systems. A brief description of each is included in the following section. A detailed description of each is included in the appendices. The pressure coring systems have also been summarized recently by Rack (2001).

SecurityDBS, BakerHughes, CorionDiamond (now ReedHycalog), and Mining Rig Coring Operations have conventional wireline capable coring systems. The wireline coring systems are useful in environments where surface temperatures are as cold (or colder) than formation temperatures. The hydrate will be stable for nearly the entire trip to the surface and only outside the stability curve for a short time period. Cores have been taken successfully in these conditions in the Mackenzie Delta.

Table 4.1 Pressure Wireline Coring – Rotary Systems

System Capabilities	Ocean Drilling Program Pressure Coring System (ODP PCS)	HYACE/Hyacinth Rotary Corer (HRC)	Pressure and Temperature Corer (PTCS)
Type of System	Rotary	Rotary	Rotary
Diameter of Core	43.2 mm	50 mm	67 mm
Length of Core	100 cm	100 cm	300 cm
Instrumentation	None, external P	None	P & T built in
Pressure Limits	10,000 psi	3,625 psi	3,500 psi
Temperature Control	None	None	Thermoelectric cooling – reliability questions
Pressure Seal Device	Ball valve	Flapper valve	Ball valve
Bit Type	9.5”x3.8” Roller cone outer bit, extended cutting shoe for soft sediment	The cutting shoe of the HRC uses a narrow kerf, dry auger design with PCD cutting elements. It rotates up to 1 meter ahead of the main roller cone bit.	
Depth Range*	6500 meter	2500 meter	2400 meter
Success Rate (% recovered)	95% core 64% pressure	50% pressure	67% latest operation

* based on hydraulic pressure & equivalent depth calculation

Table 4.2 Pressure Wireline Coring – Piston Systems

System Capabilities	Fugro Pressure Corer (FPC)
Type of System	Percussion
Diameter of Core	57 mm
Length of Core	100 cm
Instrumentation	None
Pressure Limits	3,625 psi
Temperature Control	None
Pressure Seal Device	Flapper valve
Bit Type	
Depth Range*	2500 meter
Success Rate (% recovered)	80% core 30% pressure

Table 4.3 Conventional Wireline Coring Systems – Rotary Systems

System Capabilities	Corion Diamond	Slim Hole (Mining Rig)	ODP XCB	ODP RCB	Security DBS	BakerHughes Inteq CoreDrill ™
Type of System	Rotary	Rotary	Rotary	Rotary	Rotary	Rotary
Diameter of Core		85 mm	60 mm	58.7mm	43.5/51.3 mm	43.2 mm
Length of Core	30 ft.	30 ft.	30 ft.	30 ft.	30 ft.	100 cm
Instrumentation	None	None	None	None	None	None, external P
Pressure Limits	N/A	N/A	N/A	N/A	N/A	N/A
Temperature Control	None	None	None	None	None	None
Pressure Seal Device	N/A	N/A	N/A	N/A	N/A	Ball valve
Bit Type			Integral cutting shoe 7 inches beyond bit	Roller cone with Tungsten Carbide inserts	4 ¾ and 6 ¾ HDT	9.5”x3.8” Roller cone outer bit, extended cutting shoe for soft sediment
Catcher	Custom Basket Catcher					

Table 4.4 Conventional Wireline Coring Systems – Piston Systems

System Capabilities	ODP APC	ODP APCT
Type of System	Piston	Piston
Diameter of Core	62 mm	62 mm
Length of Core	31 ft.	31 ft.
Instrumentation	None	None
Pressure Limits	N/A	N/A
Temperature Control	None	Measurement
Pressure Seal Device	N/A	N/A
Bit Type		
Catcher	Basket Catcher	Basket Catcher

4.2 Coring Systems

4.2.1 Pressure Wireline Coring – Rotary Systems

4.2.1.1 Ocean Drilling Program Pressure Coring System

The ODP system has been the most extensively tested and produces adequate core recovery in competent sediments. The PCS is capable of 10,000 psi of pressure retention, has a free fall application, and is wireline retrievable. According to ODP literature, the Pressure Core Sampler (PCS) is capable of recovering a 1.65 inch (42 mm) diameter core, 34 inches (0.86 meters) in length. The typical operating ranges are mudline to indurated formations, and up to ~6500 meters in total depth. The typical attributes of this system are given in Table 4.1.

Limitations

- Tool is limited to formations composed of soft sediments to firm clay
- Sample chamber is short to accommodate lab handling
- Core diameter is limited by ball valve size
- No standardized method for transferring pressurized cores is available
- Small core diameter could impact scientific sampling
- Wireline core recovery per meter of core is roughly ten times faster than conventional coring systems
- Problems in rough seas with drilling a 1-meter section of core

Summary of ODP Leg 204 Results

Total Deployments: 39
Cores Recovered under Pressure: 30
Average Core Recovery: 95%
Average Pressure Retention: 64%
RPM: 80-100
WOB: 5-7 klbs
Mud Flow rate: 100 gpm

4.2.1.2 HYACE/HYACINTH HYACE Rotary Corer

The rotary corer was developed by the Technical University of Berlin and the Technical University of Clausthal, and is known as the HYACE Rotary Corer, or HRC. The HRC uses an Inverse Moineau Motor driven by the circulation to rotate the cutting shoe up to 1 meter ahead of the roller cone bit. The cutting shoe of the HRC uses a narrow kerf, dry auger design with PCD cutting elements.

This design allows the core to enter into the inner barrel before any flushing fluid can contaminate the material being cored. The core diameter is 50 mm. On completion of coring, the recovery of the corer with the wireline pulls the core barrel into the autoclave, in a similar manner to the FPC, and the pressure is sealed by a specially designed

flapper valve. The HRC is designed to retain a pressure of up to 250 bar and is suitable for use in sampling lithified sediment or rock.

Table 4.2.1.2.1 Summary of HYACINTH coring on ODP Leg 204

Wireline Pressure Corer	Number of deployments	Core recovered under pressure	Hydrate core recovered under pressure
FPC	10	2	2
HRC	8	4	3

Leg 204 accomplishments:

- Hydrate core was recovered from the seabed at in situ pressure, successfully transferred into laboratory chambers without loss of pressure, then geophysically logged.
- For the first time, laboratory measurements have been made of the physical properties of natural hydrates at sub-seafloor pressures, without ever releasing this pressure.
- Some cores were then de-pressurized and the gas generated by the dissociation of hydrate was collected and analyzed.
- Other cores were preserved and transported to laboratories ashore for more detailed study. The feasibility of preserving and transporting hydrate cores to laboratories elsewhere has been demonstrated.

Future system developments include:

- Development of technologies to allow sub-samples to be taken from pressurized cores (without loss of pressure) for chemical, microbiological and petrophysical study.
- Development of equipment for performing microbiological experiments on deep sea sediment samples. Our pressure coring system allows barophilic microrganisms to be recovered from the sub-seafloor biosphere and transferred into laboratory chambers for study, without loss of pressure.
- Development of a system for electrical resistivity imaging of hydrate cores in pressure chambers. The presence of hydrates in marine sediments has a pronounced effect on their electrical resistivity.

4.2.1.3 JNOC Pressure Temperature Coring System

The Japanese National Oil Company (JNOC) Pressure-Temperature Coring System (PTCS) has passed through the development stage. In the latest coring operation, 38 coring runs were completed with recovery efficiency from 37% to 47%. Core recovery was higher in hydrate sections and poor in unconsolidated non-hydrate sections. Approximately 60% of the cored intervals maintained some pressure to the surface.

Further refinements have been made to the system and it is available for use. A second simpler system is under review for development, which can be used in soft sediments appropriate for piston coring, and in relatively stable sediments where danger of hole collapse is minimal. A review of the system is presented in the Report by Frank Rack (2001).

4.2.2 Pressure Wireline Coring – Piston Systems

For the initial 50 meters below the mudline, the sediment is unconsolidated material with little to no overburden stress. In this environment, rotary coring systems, with the use of pumped mud to remove sediments and clean the borehole, have a tendency to wash away the core while coring. To avoid removing the core material and to recover an intact representative core, piston coring systems are used. The core barrel is driven into the sediment by hydraulic pressure and plunges through the sediment until it either hits more indurate formations, or bottoms out with a full core. The core is then brought to the surface.

4.2.2.1 Fugro Pressure Corer

The percussion corer was developed by Fugro Engineers BV in the HYACE/HYACINTH Project and is known as the Fugro Pressure Corer (FPC). The FPC uses a water hammer driven by the circulation to drive the core barrel into the sediment, up to 1 m ahead of the drill bit. The core diameter is 58 mm. On completion of coring, the recovery of the corer with the wireline pulls the core barrel into the autoclave, where a specially designed flapper valve seals the pressure in the core. The FPC is designed to retain a pressure of up to 250 bar. The percussion corer is suitable for use with unlithified sediments ranging from stiff clays to sandy or gravelly material. In soft sediments it acts like a push corer.

Operational Results:

- 15 minutes for inserting tool into string
- Re-dress time 2 hours
- Good recovery in sand, gravel, stiff clay >500kPa (10 ksf)
- Good drill string stability during tests, no variation of weight on bit
- New valve design had to be fine tuned to close
- Several hydrate cores recovered still under in-situ pressure

Table 4.2.2.1 FPC Results on ODP Leg 204

Test	Recovery	Valve Plate Closed	Pressure [bar]	Heave comp P= Passive A= Active	Remarks
1	100%	-	-	A + P	Top Seal
2	50%	Ok	20	A + P	C-line Control
3	100%	-	-	A + P	Top Seal
4	95%	-	-	A + P	C-line control
5	100%	-	-	A + P	Debris on seat
6	100%	-	-	A + P	Valve blocked
7	100%	-	-	P	Valve blocked
8	20%	-	-	A + P	Liner failure
9	100%	Ok	94	A + P	-
10	100%	Ok	80	A + P	-

4.2.3 Conventional Wireline Coring – Rotary Systems

4.2.3.1 ODP RCB

The Rotary Core Barrel (RCB) is a rotary coring system designed to recover core samples from firm to hard sediments and igneous basement. The RCB is crucial for oceanic crustal hard rock studies.

Design Features

1) Rugged Design
2) Drilling with Center Bit
3) Wireline Logging with Bit Release

Limitation:

Does not recover soft sediments or granular formations (such as sand, fractured rock, or rubble)

4.2.3.2 ODP XCB

The Extended Core Barrel (XCB) coring system is used in sedimentological, climate, and paleoceanographic studies.

The XCB uses an integral cutting shoe to trim the core. The shoe is positioned ahead of the main core bit, which reduces core "washing" (i.e., core damage caused by water jets from the main drill bit nozzles). This improves core recovery and reduces core disturbance in soft to moderately hard formations.

A unique retraction device allows the XCB, which is normally extended ahead of the core bit, to retract inside the BHA until the cutting shoe is flush with the core bit. The cutting shoe is retracted to reduce failures when hard formations are encountered.

An inner core barrel swivel allows the core to remain stationary relative to the formation as the bit rotates, thereby reducing the transfer of rotary torque to weakly laminated formations. This reduces "biscuiting" (artificial layering), which is a type of core disturbance caused by transferring rotary torque to the core.

Does not recover ooze or very soft sediments, granular formations (such as sand), fractured rock or rubble, or hard igneous formations.

4.2.3.3 Slim Hole (Mining Rig) Coring System

This method uses a mineral type core barrel independently operating inside the BHA of the stationary main string. The outer barrel with the coring bit is rotated by a down hole motor driven by mud pressure. A downhole actuator system driven by the difference in mud pressure above and below the tool creates the bit load. The rotary reaction is provided by locking the actuator in the BHA. This system is used by ODP in their MDCB (motor driven core barrel) system using a positive displacement motor. The use of Mining Rig Coring Technology for hydrates is currently under evaluation.

4.2.3.4 Security DBS System

Security DBS developed a wireline system for retrieving core without pulling the drillstring. This has not been deployed for coring of hydrate sediments.

4.2.3.5 CorionDiamond Wireline System

CorionDiamond has a conventional wireline retrievable coring system that has been used extensively in Canada and the Mackenzie delta area. High quality core was recovered on Mallick 5L. Approximately 200 meters of core with a minimum of drilling induced disturbance was collected (ICDP Newsletter) from the main research well. According to Corion publications, over 97% recovery of the hydrates cored was achieved.

4.2.3.6 BakerHughes CoreDrill System

BakerHughes Inteq division has a pressure-coring device, which has been used in oilfield applications and is not wireline retrievable. This system has the ability to obtain cores from ten to thirty feet in length, much longer than the current systems employed or being developed for gas hydrate specific applications. The ten and fifteen foot core barrels available have 10,000 psi pressure retaining capability, while the thirty foot barrel is limited to 5,000 psi pressure retaining capability. Core diameters vary from 2.50 inches to 3.75 inches. As with any conventional coring system (non-wireline), trip time (temperature constraints) is too great for use outside Arctic environments. A review of the system is presented in the report of Rack (2001).

4.2.4 Conventional Wireline Coring – Piston Systems

4.2.4.1 ODP Advance Piston Corer

The ODP Advanced Piston Coring (APC) System, and the instrumented version (APCT), are designed to recover 9.5-meter long, oriented sections of continuous core. Orientation is accomplished via paleomagnetics using a downhole orientation tool located above the core barrel. According to ODP literature, the APC(T) has the following attributes:

Core Diameter: 2.44 inches (6.2 mm)
Core Length: 31.16 feet (9.5 meters)
Typical Operating Range: Formation - Very soft to firm sediments
: Depth Range - Sea floor to +300 meters below sea floor
Recovery: 100% in soft formations
APCT: Has a sensor with onboard memory for in-situ temperature measurement (-20ºC to +100ºC)

Limitations

- Does not penetrate or recover granular formations (sand) or hard ground
- Non-pressure core capable
- Can only be used in stable sediments where the danger of hole collapse is minimal

4.2.5 Conventional Coring – Drillpipe Conveyed Systems

The main problem with conventional methods is the time to return to surface (Bloys, 2001). The equipment is on the bottom of the drillstring and the entire drillstring must be pulled to recover the core. By the time the core reaches the surface, the hydrate will have dissociated. Conventional oilfield coring vendors include SecurityDBS, BakerHughes Inteq, CorionDiamond, and smaller operators.

4.3 Downhole Measurement While Coring

Measurement while coring tools are also being continuously developed and/or upgraded. A review of these tools follows.

4.3.1 APC-Methane Tool (TPC Tool)

Downhole measurement of temperature, pressure and electrical conductivity can be achieved. The device is placed in the inner core barrel and provides the information when the tool is returned to the surface for post coring analysis.

This tool was deployed on ODP Leg 204 successfully 107 of110 times.

Figure 4.3.1.1 APC Tool Schematic

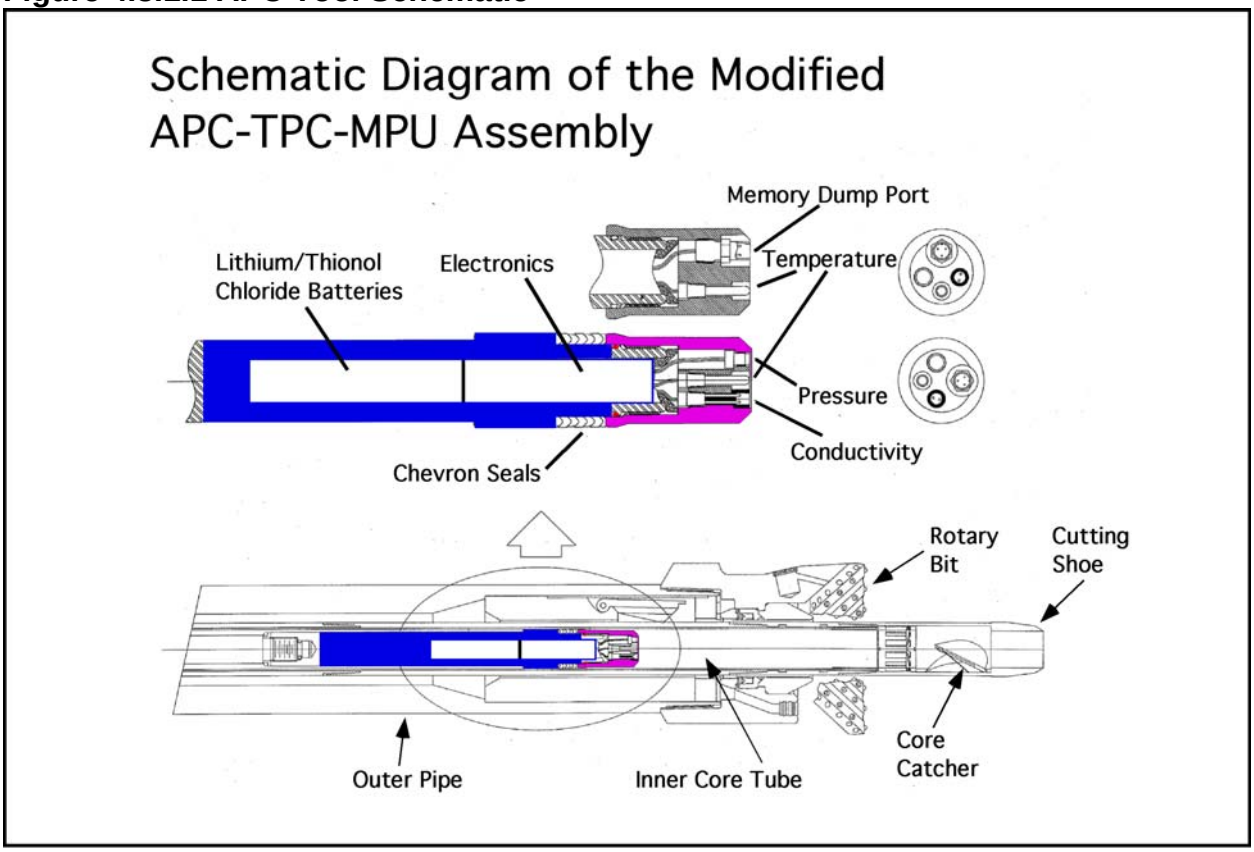


Diagram Courtesy MBARI, Bill Ussler, Pressure Coring Workshop, 2003.

4.3.2 Drill String Acceleration Tool

The Drill String Acceleration tool fastens to the top of the core barrel, records multi-axis acceleration and hydrostatic pressure, and stores the data until core barrel retrieval. The tool can be used for:

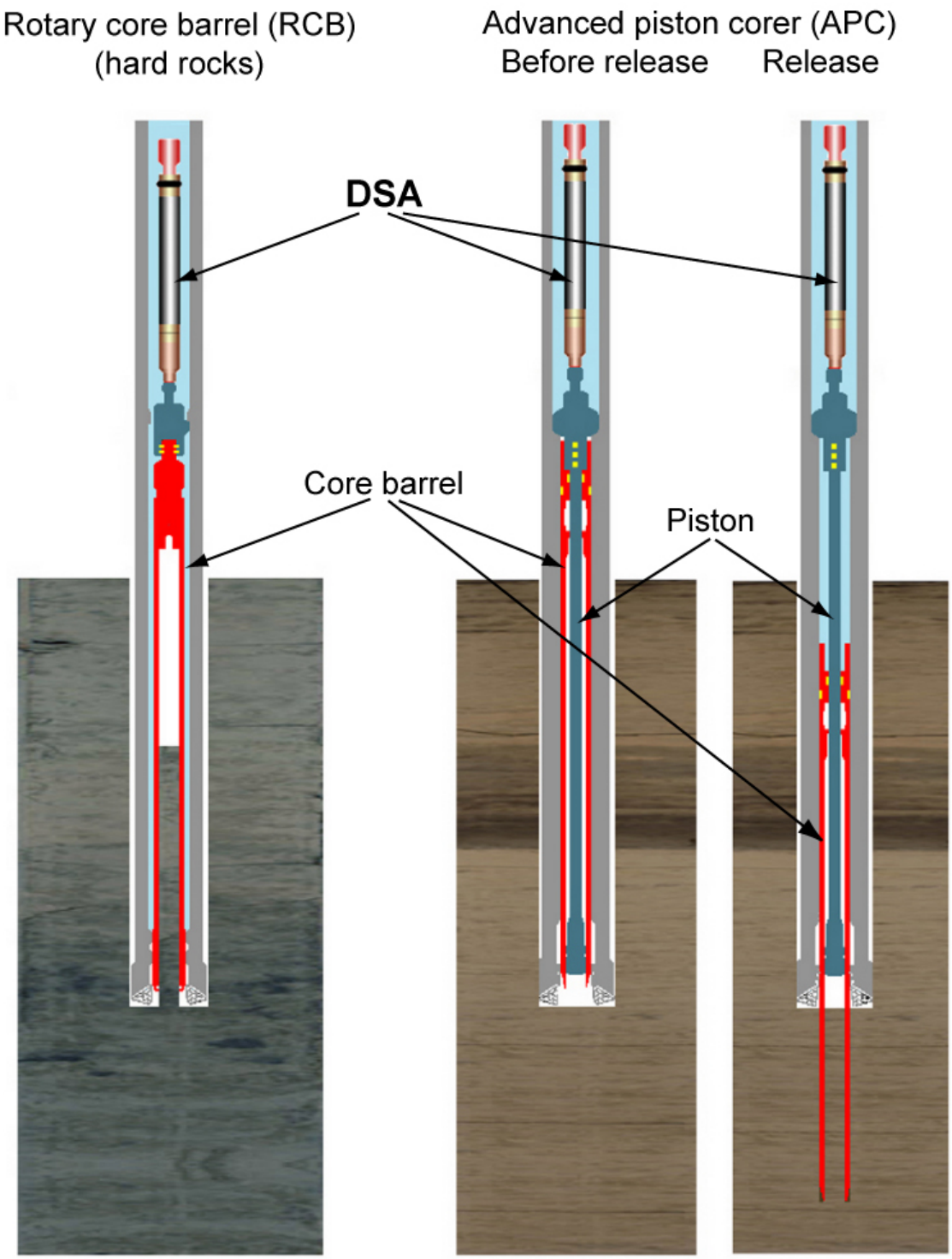
1) Downhole vs. uphole heave analysis
2) Quantification of drilling/coring dynamics
3) Formation strength evaluation

4) Pressure coring tool development

This tool was deployed on ODP Leg 204 successfully 17 of 28 times. Further development for tool reliability is ongoing.

Figure 4.3.2.1 shows a schematic of the tool in use.

Figure 4.3.2.1 Schematic of Drillstring Acceleration Tool



4.3.3 Davis-Villinger Temperature Probe (DVTP)

The Davis-Villinger Temperature Probe (DVTP) is designed to take heat-flow measurements in semiconsolidated sediments that are too stiff for the Advanced Piston Corer Temperature (APCT) tool. Coring must be interrupted to take a temperature measurement. The DVTP can also be run on wireline and hung below the bit (when the bit is off bottom) as a temperature logging tool for borehole fluids. This cannot be used for hard rocks. A full review of the tool is described in Appendix A.

4.3.4 ODP RAB-C Logging While Coring Tool

The RAB-C is designed to provide borehole resistivity logs and images (at three different depths of investigation), total gamma ray logs, and coring capabilities. This tool was first used by ODP during Leg 204 and has the capabilities of recovering 2.56 inch (6.5 mm) diameter cores. The RAB-C also provides complete azimuthal coverage of the borehole, providing high-quality resistivity images comparable to those obtained with the Formation MicroScanner (FMS). These data will provide visual recognition of igneous layers as well as the identification of fracture patterns, structural orientations, and formation thicknesses.

RAB-C was deployed 8 times on Leg 204 and recovered 31.1% of the cored intervals.

4.4 Summary

There are still several limitations of the existing equipment on gas hydrate coring or operations. Whether conventional coring, conventional rotary wireline, or Mining Rig Coring systems can provide competent hydrate core recovery in an offshore environment is unclear. These systems provide neither pressure core containment nor temperature control to maintain hydrate equilibrium and prevent dissociation. The conventional rotary wireline and mining rig coring systems would be adequate for Arctic environments based on experience in the Mallik's coring operations.

Currently, the ODP coring systems can be applied for the bulk of the coring use in marine environments. However, from the standpoint of returning non-dissociated gas hydrates in a pristine condition to the surface, they do not appear to have been consistently successful. Also, core length on the pressurized barrels is limited to approximately one meter. From an oil and gas industry perspective, where one is accustomed to greater core lengths and recovery efficiency, the coring operation is not satisfactory.

5. CORING OPERATIONS

5.1 Operator Representative for QC/QA

Very detailed protocols should be established and Quality Control (QC) crosschecks at each step, wherever possible. The operator's core analysis specialist, lead core analysis lab representative, and hydrate experts should be involved in documenting the core analyses procedures. The operator representative will have to be available continuously.

5.2 Mud Systems

Coring fluids are typically water-based mud. In order to avoid a) dissociation of the hydrate and b) reduction in borehole quality, the mud should be kept cool, within the hydrate stability zone (see hydrate dissociation line in Figure 3.1 as a reference for the temperature and pressure targets). In unconsolidated sediments, hole quality can be difficult to maintain. A chilled mud with a hydrate promoter assists in maintaining a gauge hole, although it can lead to contamination of the core. Care must be taken in the decision to use a promoter. Shale stability additives may also be required in immature clay-rich sediments.

5.2.1 Mud Additives

Due to the nature of the sediment, the shallow depth and low fracture gradient, only a few additives can be used. Mud weight needs to be kept below the fracture gradient. Much of the drilling coring operations are riserless, thus the need for minimal chemicals returning to the ocean floor. Chemicals used to delay dissociation including lecithin, polyvinyl pyrrolidone and polyvinyl caprolactam, have been used in coring operations. These are added to the mud to prevent dissociation in the near wellbore area. The result is a gauge hole better suited for wireline logging purposes.

5.2.2 Gas Hydrate Formation in Mud

In deepwater drilling, caution should be taken to prevent hydrate formation in the mud (Whitson and McFadyen, 2002). Therefore, the downhole environment can be designed to make hydrate less stable by mixing salt and/or glycol into the mud. About 5wt% of NaCl or KCL are typical values of salts in a low-weight mud. However, when the hydrate-bearing formation is penetrated, the hydrate in the sediment should be kept stable for hole stability, core recovery, and safety. To achieve both contradictory requirements, the kinetic stability of hydrate should be studied. Experiments have been performed in the past to see the effects of lecithin, polyvinyl pyrrolidone, and polyvinyl caprolactam on gas hydrate stability. Results show that polyvinyl caprolactam is the most effective material for decelerating both hydrate formation and dissociation (Takahashi et al, 2001). Note that in Mallik's well testing, lecithin was used to promote hydrate stability (Uchida et al, 1999).

If polyvinyl caprolactam mud is used in a cased off hydrate zone, unsafe gas pressures may develop from hydrate dissociation if the mud temperature is too high. To prevent such problems, mud-cooling systems must be used. Return-mud temperature at the hydrate zone should not exceed the hydrate equilibrium temperature at the drilling depth. However, if the required layout is too large for a particular rig, a smaller capacity system may be used if it is carefully monitored and operated through a booster line, in conjunction with additional surface mud circulation (Takahashi et al, 2001).

During the drilling process, analysis of the return mud can provide evidence for the existence of gas hydrate. Mud samples taken at the well site can be placed in a container to obtain headspace gas that can then be analyzed for methane content by gas chromatography.

5.3 Coring System Initialization

Typically, a wireline device is gravity fed through the drillstring and lowered in place. Pump pressure seals some of the wireline instruments. Coring can commence after an increase in pump pressure at the surface indicates a proper connection.

5.4 Coring Parameters

Coring operations need to be conducted with a near constant weight on bit, as quickly as possible, and around 100 RPM for soft sediments. Trip times to the surface need to be as fast as possible (~ 400 ft/minute) if the goal is to preserve hydrate. If dissociation starts and the core is unconsolidated, the expanding gas can severely disrupt the core.

5.5 Pressure/Temperature Coring

Once the core tops out in the barrel, the bit is lifted from the bottom, the pulling device is sent to the bottom, it latches onto the pulling mechanism, and the barrel retracts, allowing the ball valve or flapper valve to close. Pressure and temperature conditions are recorded, the valve closed, and the sample pulled to the surface as quickly as possible.

5.6 Wireline Out

A retrieving tool is sent down the hole within the drillpipe. The tool latches onto the core barrel assembly, releases the catch mechanism and allows for removal. The core barrel assembly is pulled to the surface as quickly as possible, ~75-150 feet per minute.

5.7 Core Laydown

The ChevronTexaco Low Invasion Coring Manual, a reference for a conventional coring system, describes the use of a core brace or shuck. The shuck is a device for keeping

the core from bending. Bending can damage the core by causing fractures in the rock. Depending on the objectives of coring, the hydrate cores may be subjected to a modified version of this protocol.

The core must be transferred from its vertical position on the rig floor to a horizontal position in the core processing area. During this maneuver there is the risk of flexing the inner barrel and cracking the core inside. The simplest way to avoid this problem is to slide each 30-ft. section of inner barrel into a rigid protective sleeve or “shuck”, usually a 30-ft. section of 7-inch casing. Most of the descriptions that follow assume the presence of a shuck. However, if a shuck is not available, the core can be lowered without flexing, using two nylon slings (each placed 7-½ ft. from the ends of the 30-ft. inner barrel section), as presented below. A detailed procedure is included in Appendix B.

The short cores typically obtained in hydrate coring operations are at less risk of flexure damage; however, all cores should be handled in a way to minimize flexure damage.

The process of getting the core from the coring apparatus to a horizontal, workable surface is the most challenging aspect of the procedure. This needs to be done as quickly as possible. If the coring apparatus needs to be placed for storage, even up to 5 minutes, consider placing cooling systems in the storage location to minimize further hydrate degradation.

6. CORE HANDLING, HYDRATE VERIFICATION TESTS AND CORE PROCESSING

In many cases, poor handling procedure at the surface can negate a good coring operation. The final objective of the coring and analysis program must be incorporated into the procedure for proper core handling at the wellsite. Most laboratory tests are sensitive to sample conditions because poorly consolidated material can easily be altered during the initial handling process. General considerations for any core are given below.

- Communication between all drilling and core handling personnel is essential
- All safety precautions should be implemented
- Carefully handle core at all times to reduce disturbance
- Use a “shuck” or a core brace to avoid core flexure during handling of long sections
- Use a wheeled boot with laydown of a long core section (30’) from the rig floor
- Speed in handling cores is essential
- Remove the coring equipment from the wireline equipment
- Remove the core barrel from the coring equipment
- Lay down the core barrel on the rig floor if study objectives and safety permits
- Immediately place the core barrel in a controlled temperature environment (~32 ^{o}F)
- Inspect the core for hydrates
- Section the core for analysis

The presence of hydrate is a safety concern. High pressure dissociating hydrates can lead to sediment being forced out of the barrel upon dissociation. Core barrel stabilizers or other safety devices may be necessary to avoid movement of the barrel upon release of pressure.

Evaluation of core for Hydrates is essential:

- Visual observation coupled with infrared temperature readings and pressure readings, will give information on hydrate condition.
- Temperature reading can be taken using a) an infrared video camera for a profile of the core and/or b) a series of temperature probes to provide a thermal profile of the core.

Once the core is at the surface and depressurized, remove the core from the core barrel. Visually inspect the core for hydrate, ice, or gas bubbles coming from the pore space. Note the depth of observed hydrates. Using an infrared camera system, evenly walk the length of the core obtaining a digital image log of the core temperature. Again, note areas of suspected hydrate. Carefully cut a small section of core, measure the dimensions and place in a bucket–type apparatus with inverted gas collection device to test for gas evolution. Collect the gas and measure its volume.

A natural (total) gamma attenuation log can also be recorded to determine sand-shale zones. Spectral gamma reading can be measured under different conditions when fast preservation time is not important. Spectral gamma logging is typically too slow for most hydrate preservation objectives.

Once the gamma log and all other immediate tests on the whole core have been completed, section the hydrate areas with a cutting saw and place the sub-samples for preservation in pressure vessels or liquid nitrogen. The pressure vessels can be either aluminum or stainless steel, marginally larger than the core diameter, able to handle dry ice temperatures, rated for pressures well above the hydrate formation pressure, and easily capped. High-pressure aluminum vessels are recommended if computerized tomography (CT) scanning of the cores are to be performed. Methane can then be injected into the sample container to maintain the pressure and preserve the hydrate. Other non-flammable gases, such as nitrogen, may also be used to pressurize samples for safer transfer under controlled temperature and pressure conditions. Some gases will form hydrates at pressure and temperature conditions different from methane.

There is no universally accepted method for transporting gas hydrate samples. Some types of analyses are not adversely affected by storage at very low temperatures, for example, in liquid nitrogen. Other analyses can be greatly compromised. Storage in a compressed hydrate-forming gas environment has the potential for forming additional hydrate. This may or may not be acceptable for individual project goals. Storage of methane hydrates in a gas other than methane may actually promote dissociation although samples from the Mallik 5L-38 program were successfully stored and transported using a combination of pressurized nitrogen and dry ice temperatures.

The whole core sections can also be placed into similar vessels with Viton rubber sleeves (or equivalent to handle the low temperatures), electronic and acoustic instrumentation included in the flow distribution heads, and capped off.

6.1 Core Processing

For analysis of hydrate bearing sediment, wellsite analysis is recommended.

6.1.1 Wellsite Analysis

Due to the nature of natural gas hydrate bearing sediment, it is recommended that the hydrate bearing sediment be analyzed at the wellsite. Details of the analysis are elsewhere in this document.

6.1.2 Conventional Core Analysis Procedures

Usually, the most cost efficient approach is to process the core into 3-foot (or 1-meter) capped sections and then forward it to a laboratory for analysis. Since the effect of storage on hydrate-sediment mixtures is essentially unknown, storage times prior to core analysis should be minimized.

6.2 Pressure Core at Surface

Pressure coring equipment must be checked for preserved conditions. Immediately record the pressure maintained in the barrel, place the core barrel in a container such that original formation temperature is restored, and the pressure recorded. If gas must be bled off to reduce pressure, the gas must be collected for future analysis. Record core temperature continuously, if possible. The core should be removed from the barrel and sectioned for further analysis.

Freezing of core will disrupt the structure of fine-grained sediment, but it may be the only method to preserve coarser-grained sands. If sediment samples are needed before freezing, care must be taken to minimize sample disturbance. Deep freezing to liquid nitrogen temperatures is acceptable if the core sample will not be appreciably warmed prior to analysis. However, evidence exists that deep freezing may actually enhance hydrate dissociation if the sample is significantly warmed. Therefore, deep freezing should be avoided if possible.

6.3 Atmospheric Core at Surface

Cores taken by conventional wireline methods will have depressurized or dissociated hydrate by the time they reach the surface. Care must be taken to avoid unneeded hazards due to the presence of methane and other gases (such as hydrogen sulfide). Temperature controlled field laboratories can be used to minimize the heating of the hydrate bearing sediment. The unit can be controlled to 0-4 ºC and all necessary work can be conducted at that temperature.

Conventional oilfield operations use dry ice trays to freeze the samples before cutting. If unconsolidated coarse-grained material is expected and the hydrate has dissociated, freezing to dry ice temperatures may be warranted before further handling. The personnel handling the core at the surface must be fully aware of the safety hazards associated with dry ice handling.

If some hydrate has been retained, the core must be cut into sections, placed in containers, bags or wraps for immediate testing, deep freezing, pressurized storage or transportation. Appropriate containers are still under evaluation for transportation and storage.

7. WELLSITE CORE ANALYSIS AND PRESERVATION

7.1 Onsite Analysis of Gas and Gas Hydrate

Mobile core analysis units can be setup at the wellsite or on a drillship. Use of the whole core sections of hydrates for analysis is recommended. Place the whole core piece in the measurement equipment. Multiple test types can be conducted in the same coreholder. Acoustic velocity, electrical resistivity, and geomechanics can be tested simultaneously. If the core holder is made of CT scan-able material, the core can be CT scanned upon arrival at the laboratory. NMR requires unique materials for testing and can be incorporated into the program. This limits the sample size to 1 or 1.5-inches in diameter, or smaller. NMR logging the whole core at the wellsite, along with the gamma log, is the best alternative. Temperature profile measurement on the sample within the pressure vessel may be necessary for proper hydrate verification.

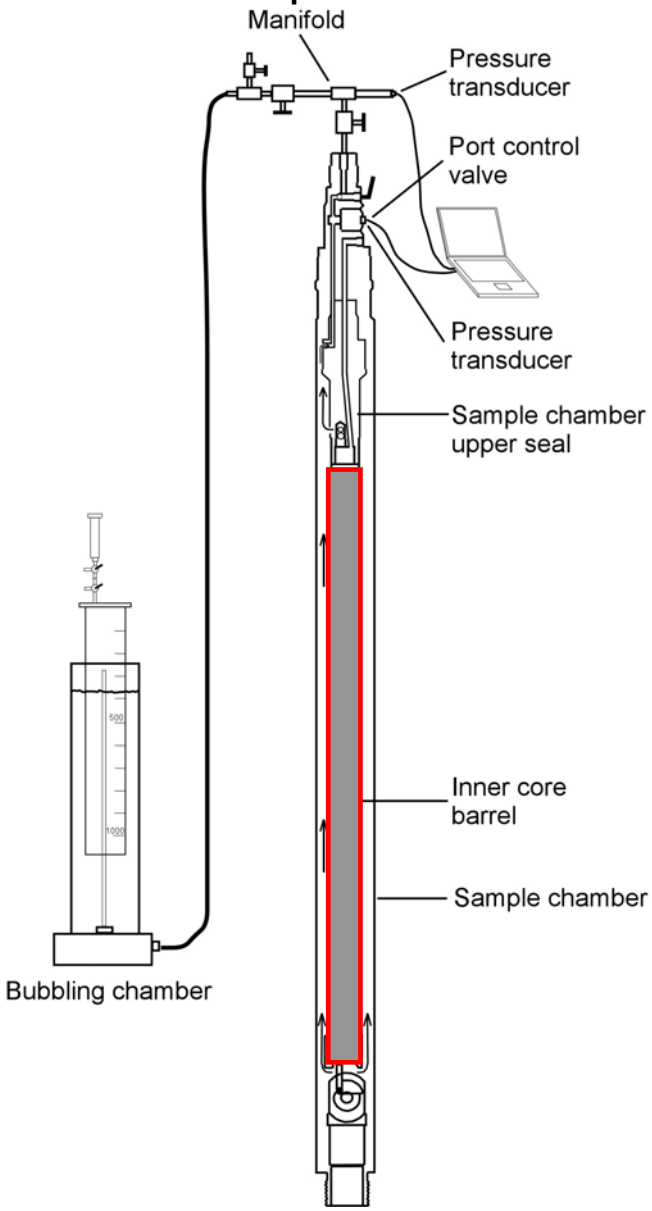
7.1.1 Ocean Drilling Program Floating Drillship/Laboratory Joides Resolution

The ODP operated Joides Resolution Drillship can be setup as a floating gas hydrate analysis laboratory. Apparatus included on the ship can be reviewed in the Leg 201 or 204 post-cruise technical notes. A brief review is included here. For pressure cores, the use of the Pressure Core Sampler (PCS) has been successful in recovering in-situ gas, measuring gas volume and taking samples for composition and isotope analysis. A schematic is shown in Figure 7.1.1.1. The pressure core sample is depressurized over time, at various pressurization rates. The pressure, temperature, gas volume, and gas composition are measured with respect to time.

Pressure Core Sampler Leg 204 Results (Milkov, 2003)

- 37 cores were deployed
- 30 cores were recovered under pressure and degassed (81% success rate)
- Pressure measured on deck: 36-169% of in-situ pressure
- Depth of recovered cores: 14-292 mbsf
- Time of degassing: 334-11,268 minutes
- Volume of collected natural gas: 0.09-94.5 L (usually ~99.9% methane)
- Core length: 0.23-1.00 m (most cores >0.9 m)
- C_1/C_2 ratios for in-situ gas is higher than for headspace gas

Figure 7.1.1.1 ODP Pressure Core Sampler



7.1.2 HYACE/HYACINTH Wellsite Analysis

The HYACE/HYACINTH Project developed techniques for transferring pressure cores to pressure vessels, while maintaining the in-situ pressure. The equipment used in this process is described in more detail in Appendix B. The result is a core under pressure that is removed from the core barrel and can be analyzed.

Analysis includes the use of the Vertical Multi-Sensor Core Logger for measurement of electrical resistivity, magnetic susceptibility, P-wave velocity and Gamma Density.

7.1.3 Onshore Mobile Core Analysis Laboratory

For onshore analysis, a mobile laboratory can be deployed. The HYACE/HYACINTH equipment can also be used. However, a trailer-based setup can be constructed and outfitted with all the necessary measurement equipment. Anadarko/Maurer used a mobile facility during the arctic hydrate drilling. The mobile laboratory included equipment to measure whole core gamma, digital photography, grain density, porosity, permeability, whole core acoustic velocity, shear and compressional velocity, resistivity, mineralogy, grain size distribution and mercury capillary pressure. Additional equipment included CT scanner, infrared photography, thermal conductivity, whole core NMR, and dissociation test apparatus.

Anadarko/Maurer plan to preserve every other foot of core in pressure vessels for future analysis. Velocity analysis of the samples will be conducted to locate the hydrates.

7.2 Hydrate Identification

When the core arrives at the surface, a visual inspection of the core should provide first estimate of whether the core contains gas hydrate. Gas hydrate is unstable at surface conditions and requires special sampling strategies to characterize the gas hydrate and to assess the amount of gas hydrate occurring in the cores. Using the experience from Leg 164 of ODP program and Mallik 2L-38 well program, the following procedures can be employed to analyze the gas hydrate characteristics and evaluation.

As soon as cores arrive on deck whole-round sections that are thought to contain gas hydrate should be immediately taken for both shipboard and shore-based analyses. Gas voids in the remaining cores, when present, are then sampled by means of a vacutainer for analysis, as part of the shipboard safety and pollution prevention programs. Core samples are taken for biostratigraphic analysis. When the cores are cut into sections, whole-round samples should be taken for shipboard interstitial-water analysis and for shore-based studies of organic geochemistry, microbiology, thermal and physical properties. Headspace gas samples should be immediately taken from the end of cut sections and sealed in cans, and in glass vials, for light hydrocarbon analyses. One section per core is commonly taken and sealed in a tube equipped for measuring core temperature, total volume, and composition of gas evolved from decomposing hydrate.

Note that all vessels and test materials need to be ready for use before the core arrives at the surface. The technicians should arrive ~2 days (3, if fully processing on site) before the first core arrives at the surface. This allows time to check equipment, take safety training, set up a core processing area, pre-label crates, sample bags, etc. The primary job for the technicians is carrying out the core lay-down, mark-up, cutting, sampling, purging, capping, crating, cataloging and shipping process. The technicians usually oversee the logistics issues of getting the core shipped out as soon as possible, as well as alerting the lab of the expected arrival times. Extra help is usually needed with cutting the core, moving the crates, etc.

Cores should be further checked for indication of gas hydrate such as gassy, self-extruding cores, and cold sediment with lighter coloration. When gas causes the sediments to extrude from the core liners, core liner extensions are attached to 1.5 m long core sections to maintain the stratigraphic position of the sediment. After the core is split, the original liner and extension are sealed together with acetone (Rack, 2001). Unsplit core sections are run through the multisensor track and thermal conductivity is measured on sections relevant for heat flow studies. Because gas hydrate decomposition is endothermic, low temperature thermal anomalies may be associated with gas hydrate bearing sediments. Therefore, a variety of thermal measurements should be made on recovered cores. Cores are then split into working and archive halves from bottom to top, so one should be aware that older material has been transported upward on the split face of each section. The working half of each core is sampled for shipboard analysis (such as physical properties, carbonate contents, and bulk x-ray diffraction), and for shore-based studies. Both archive and working halves of the core should then be put into labeled plastic tubes, sealed, and transferred to cold storage space aboard the ship.

Sub-samples must be identified with site, hole, core and depth information. The sediments can be classified into nonbiogenic, biogenic, mixed, chemical, lithified, etc. depending on the sedimentological system used.

In the most recent drilling operation in the GOM (ODP Leg-204), the additional technical capabilities were tested to collect gas samples for analysis, and water samples from 550 feet below the seafloor, for water geochemistry. Physical and chemical tests on the cores were conducted onboard. The temperature at the ocean floor was about 35.6 ^{o}F. Temperature and pressure of the cores were logged.

7.3 Core Temperature Measurement System

Temperature paths of core samples from their *in situ* temperatures, to the conditions onboard of the drillship, are complicated. During the drilling process, frictional heat warms the cores by an undetermined amount, even though the bit is being cooled by sea water that pumps down the hole at near seafloor temperature (< 39 ^{o}F). During core recovery the sediments are first exposed to cooler temperatures, with the minimum temperature being near the seafloor (< 39 ^{o}F). Appreciable warming does not start until the cores pass through the ocean's thermocline on the way to the surface and continued warming occurs once a core arrives on deck. For Blake Ridge well, the surface sea water and ambient air temperatures were about 79°F and 70°F ± 9 ^{o}F, respectively (Rack, 2001).

A thermocamera, which is a hand-held device, can be used to measure the infrared spectral transmission as an indicator of system temperature. This can be used only onshore or topside offshore with air between detector and the suspected hydrate, since water absorbs infrared transmission.

Temperature measurements of cores on the catwalk of Blake Ridge operation were in the range 50 ^{o}F to 59 ^{o}F (Rack, 2001; Zuidberg et al, 1998). In some cases, unusually low temperatures can be recorded. This anomaly can be attributed to heat of adsorption during endothermic dissociation of hydrates in the sediment. During ODP Leg 204, sediment surface temperature heterogeneities of longitudinally split cores were measured in 20 cm intervals. A 30-channel thermocouple digital thermometer measured temperature anomalies caused by the dissociation of disseminated gas hydrate within 10 minutes of splitting the core. The instrument consisted of 30 thermocouple probes connected to a 3-channel analog digital converter data logger controlled by a laptop PC. A plastic holder with an independent spring, allowing all the probe heads to touch uneven areas on the sediment surface supported each of the probes. The 30 probes were spaced in a moveable grid of five rows across six columns, spaced at 10 mm intervals along the section. The data acquisition system automatically recorded the temperature at each of 30 probes every 2 s for a total of 40 s. The surface of 20 cm long core was measured by moving the probe array so that the operation was repeated in three positions, giving 90 discrete temperature measurements. The resolution and accuracy of the probe were 0.2 ^{o}F and 0.9 ^{o}F, respectively. An independent portable digital thermometer was used to monitor the temperature 2 cm below the surface, as an overall indicator of sediment temperature.

Further onsite analyses of the cores should be performed when possible. For example, measure the properties using a process similar to GHASTLI of USGS (Winters et al, 1999, 2000, 2002), and a recently developed Temperature-Pressure-Conductivity (TPC) tool, which can continuously record temperature and internal pressure in the headspace at the top of a core, during its ascent to the surface. These tools will allow systematic measurement of thermodynamic processes in gas rich marine sediment cores (Ussler et al, 2002).

7.4 Spectral Gamma-Ray Measurements

If possible, spectral gamma-ray measurements should be conducted while the core is still preserved in the aluminum inner barrel sections. The core gamma unit should be calibrated with a 200 API gamma ray emitter before every core is tested. Gas hydrate is detected by anomalies in the digitized and plotted gamma ray response. A gamma-ray densitometer uses an emitter and a sensor. The transmission of gamma rays to the sensor is a function of the density. Because densities of hydrate and water are very similar, gamma ray densities alone cannot discriminate between the two. However, gamma ray measurements can indicate changes in conditions that can be hydrates.

7.5 Gas Hydrate Dissociation Pressure System

Gas hydrate dissociation pressure systems include a sample holder, gauge block, pressure gauge, and manifold assembly, and can be used to analyze dissociated gas and pore water. Gas hydrate samples are placed in the sample container and the entire manifold assembly is evacuated in 1 second. Samples are dissociated at room temperature, releasing gas into the gauge block. After thermal equilibrium and complete decomposition, the resulting pressure and temperature are measured and the gas is sampled through a port. The composition of the gas can be determined by gas chromatography. The resulting water is analyzed for dissolved constituents and isotopic composition.

7.6 Gas Collection System

In this analysis, chambers are used to collect the gases that evolve from core sections, and to monitor the temperatures as the core warms (Paull et al, 1996). Sections of the core are placed in 1.54 m tubes that are slightly larger in diameter than the core liners. The tubes are constructed from standard polyvinyl chloride schedule 40 pipe sections (3.5 inch), with end caps that are machined so they seal on both ends with O-ring fitted plates. These can be bolted on quickly to make a gas tight seal. Thus, all the gas that is evolved within the cores (after they are sealed in the tubes) can be collected and measured.

Gas volumes can be measured in three ways. At one end of the gas collection tube, the sealed end caps are fitted with a port through which gas can flow out of the tubes into Tygon tubing that runs through OMEGA flow meter. The flow meter is calibrated to measure flow rates in the range 0-2 L/min and the output of the flow meter is recorded every 2 seconds. This provides a continuous monitor of the flow rate at which the gas was passing from the tubes. The rate is integrated with respect to time. The gas tube is then passed into overturned 1-L graduated cylinders that float in baths of salt-saturated water. The cylinders are filled with the gas as the gas exits the tubing. Because the cylinders were initially completely water filled, the volume of water that is displaced by the gas can be measured directly. The cylinder tops are fitted with luer-lock fittings, which allows the gas to be collected in 60 ml syringes. This gas is then available for compositional analyses.

Temperature measurements are made by inserting a thermistor from 4 to 8 cm into the cored sediment through a predrilled hole in the core end caps. Thus, temperature is monitored within the cored sediments inside the gas collection tubes. The temperature measured on each probe is automatically recorded every 2 seconds, using a digital transmitter that is integrated with a Lab View program.

7.7 Gas Hydrate Sampling for Post Cruise Analyses

7.7.1 Pressurized and Frozen Samples

To confirm the crystal structure, composition and cage occupancy of natural gas hydrate, samples of gas hydrate are collected and stored in containers for post-cruise analysis. Pressure vessel assemblies consisting of a gauge block, gaskets able to seal at low temperature, a pressure gauge, a pressure transducer and a manifold are used to ship samples to the lab. To minimize the decomposition of gas hydrate during storage and shipping, the dead space within the pressure vessels can be filled with fine glass beads (1mm ID). Pressure vessels can be stored in a refrigerator or freezer at temperatures that are stable for the respective pressure and gas hydrate structure. They can be shipped in an insulated cooler filled with dry ice or other cooling system that abides by applicable safety guidelines. Pressure vessels containing flammable gas must be Department of Transportation (DOT) certified or posses a DOT waiver. Individual gas hydrate samples can also be wrapped in aluminum foil, stored, and later shipped in liquid nitrogen to the lab of destination.

7.7.2 Samples for Gas Hydrate and Sediment Test Laboratory Instrument (GHASTLI) Testing

GHASTLI has the capability of recreating sub-seafloor pressure and temperature conditions, while measuring gas pressure generation, acoustic velocities, permeability, electric resistivity and shear strength (Booth et al 1994, Booth et al 1999, Winters et al 1994, 1999, 2000, 2002). Whole round sediment sections containing significant gas hydrate were cut into lengths of either 13-14 cm, or 27-28 cm, using an ODP type rotary core liner cutter and a wire saw. The liner is immediately capped on each end and quickly transported to the laboratory, where the sample is placed in a thick-walled stainless-steel pressure vessel (PV) that measures 7.62 cm ID x 27.9 cm inside length. Other sized pressure vessels have also been used to transport field samples for GHASTLI testing. In-situ pressure is restored to the sample by pushing ultra-high grade gas (typically methane) into the PV with a gas booster, or by simply using the pressure from commercially available gas cylinders. The re-pressurization technique requires 10 minutes to complete. The preserved samples are then refrigerated or frozen for transport to the facility for GHASTLI testing.

7.7.3 Handling Pressurized Core

Typical procedures associated with gas hydrate containing core is to measure or estimate recovered and in-situ pressure and temperature, return the core to stable temperature condition (if possible) allow the pressure to decrease, measure the volume of dissociated gas, and collect the dissociating gas. The core is then cut into sections for further analysis. The HYACE/Hyacinth group, as well other groups are developing systems to maintain pressure and temperature of the hydrate core for analysis. This is designed to work with the pressure-coring device and move the samples from the core

barrel into analytical equipment without losing pressure and temperature. Natural Gamma Ray, acoustic properties, etc. can then be measured on the whole core section.

7.7.4 Slabbing

Core slabbing is typically done for geologic and photographic purposes. For the small diameter wireline hydrate cores, slabbing is not recommended. Slabbing should be done only after all immediate analyses are completed. Freezing of unconsolidated material is necessary for proper slabbing. Freezing to dry ice temperature (or lower) is recommended. A horizontal bandsaw is helpful for high quality slabbing of unconsolidated sediment and prevention of lost material.

7.7.5 Plugging

Freezing of soft sediment and plugging is recommended to prevent sample deterioration. Follow the routine procedure to deep freeze the core, rig up the liquid nitrogen to the drill press, and cut the plugs using liquid nitrogen as the bit coolant. Problems may occur using liquid N2, due to mixing with methane in the hydrate. Sample hydrate stability conditions may change however, they can be monitored using the known conditions of methane and nitrogen gas hydrates. For tests that require as little alteration as possible, the use of full diameter equipment is recommended. If plugs are to be used, the use of liquid N2 is currently the best technique for drilling samples.

Plunge core cutting can also be used to obtain samples. The reliability of this type of core cutting is varied. Proper continuous pressure is necessary to avoid cutting induced sample heterogeneity. CT scanning can verify sample quality and homogeneity. This is especially important for geo-mechanical testing.

7.7.6 Sample Handling

Depressurized and thawed samples destined for routine property measurements (such as, water content, grain density, porosity, and air permeability) can be handled at room conditions. Soft sediment samples can be stored in original liners, or may be encased in nickel foil, heat shrink Teflon® or Teflon® tape to prevent loss or deterioration.

Depending on the type of analysis to be performed, some samples may be frozen to dry ice or liquid nitrogen temperatures, and wrapped with nickel foil, wrapped with Teflon® tape and nickel foil, or wrapped in Teflon® tape. Stainless steel screens can be used on the flat cylinder surfaces.

7.7.7 Core Analysis Laboratory Equipment

Equipment for measuring routine rock properties and petrophysical properties of hydrate bearing sediments is recommended for the facility. The equipment is discussed in further detail in Section 9 of this manual.

8. CORE TRANSPORTATION AND MONITORING

Transportation of gas hydrates in pressurized containers must be performed with the utmost caution. Vessels should be constructed using ASTM protocols and OSHA standards, pressure tested at conditions to 1.5 times the maximum working pressure of the container, and rated to DOT standards. Air transportation is suitable for dry ice or liquid nitrogen shipping containers, or when non-flammable gas is used for pressurization. The ground transportation for custom vessels and small vessels need the current DOT certification. In a recent experience during the Leg-204 operation, it was very difficult to get approved pressure vessels. One could get a one-time waiver for small quantity similar to DOT specification (Rack's experience, 2002).

8.1 Shipping to Core Analysis Lab

Rapid shipment of the core to a lab can take many forms. If the drilling operation is offshore, the options are to transport the core by helicopter or workboat. In many cases the workboat option is too slow, and shipping the core by helicopter is the only viable option, where the weight and space limits of the helicopter must be met. A representative sample of the crates should be weighed on a job-by-job basis to obtain a more accurate estimate of the number of core boxes the helicopter can carry. Care should be taken to give the rig supervisor as much lead-time as possible for helicopter planning.

A log should be made detailing the contents of each crate. Each crate lid should be labeled with the well name, core number, core depth and destination lab address.

Once the core reaches the helibase/shorebase, the process becomes similar to transporting the core from a land rig. The shipment must be met and trucked to either a local lab, an airport for further transport, or placed on a truck for overland shipping. Air schedules must be determined well in advance in order to minimize delays. Adequate freight space on the plane must be reserved as far in advance as possible. Careful investigation must be done to determine the type of documentation needed for sending the cores by airfreight. The core must be met on the destination end and transferred to the lab. Care must be taken to avoid any temperature extremes.

Once the core reaches the lab, processing should begin immediately (regardless of time of day/night) and should continue until all planned work is completed.

In some cases there is neither room on the rig for processing, nor a way to get the core quickly to a lab at a rational cost. In these cases a temporary core processing facility can be established.

8.2 Pressure Core

Aircraft should not transport pressurized core samples. Land or sea transportation is recommended, although sample integrity may decline with time. Proper sample stabilization should be performed on the rig prior to transportation. Pressure and temperature recording and monitoring devices should be included on the transportation equipment for a record of sample history. Stainless steel or aluminum vessels with burst plates or vent valves are recommended. Transportation in an open-air vehicle is appropriate. Leaking gas from the pressure vessel into a closed container vehicle may produce a dangerous condition. All logistics should be consummated prior to the coring operation.

8.3 Atmospheric Core

Core transportation in the oilfield typically uses insulated metal crates capable of handling three-foot long core tubes. The crates can be packed with dry ice and hold 30-60 feet of core. The crates have been designed to hold the weight of the core and be easy to incorporate into rig operations. The frozen stabilized core can then be sent to a laboratory for processing and storage. This procedure can be applied to hydrate cores if proper safety precautions have been taken for the presence of methane.

8.4 Safety Concerns

The transportation of hydrate cores involves several issues related with safety. These are: (a) pressurized core barrels may cause liner explosion, and sediment shot out of barrel, (b) dangerous gases, (c) airline regulations relating to the description of gas hydrate issues, and (d) over road regulations relating to commercial versus private transportation.

9. LABORATORY CORE PROCESSING, HYDRATE VERIFICATION and CORE ANALYSIS

Laboratory experiments provide an opportunity to investigate the characteristics of gas hydrate in porous sediments, under controlled environmental conditions. However, the "preserved" nature of the sample should be quantified and verified. Preserved samples are defined as those that have been kept at formation pressure and temperature. Samples that have been depressurized, but kept in the hydrate stability region, can be classified as self-preserved or restored. There are mainly two kinds of materials used to study synthetic gas hydrate in porous media: (1) a synthetic porous medium like silica gel, engraved plates, or reconstituted sand grains (Handa and Stupin, 1992; Anderson et al, 2001; Buffet and Zatsepina, 2000), and (2) a natural porous medium, which is typically a consolidated sediment sample (Booth et al, 1999, Dallimore et al, 1999).

Physical properties measured in gas hydrate dissociation experiments conducted on core samples in the field indicate that less than 40% of the pore space was occupied by gas hydrate, whereas in-situ values may be higher than 80%. The impact of storage on the gas hydrate samples must be considered in any laboratory test program.

In general, the properties to be tested in the laboratory can be included as dissociation-formation kinetics, mud stabilizer analysis, the hydrate thermal properties, conductivity, heat capacity, geo-mechanical tests, and acoustic properties. Tests may be performed on intact cores that were maintained in pressure-temperature stability zone. Material characterization of each sample is necessary. Characterization may include uni-axial consolidation, geo-mechanical variables, permeability tests, creep tests, pore pressure tests, and hydrate structure tests, among others.

In this section we discuss the laboratory measurements of the above important properties of gas hydrates in cores. Most of these experiments can be tailored to the special gas hydrate core samples. Some of the tests discussed in Section 7 are equally valid for the regular laboratory analysis, and we will further elaborate on them, as needed.

9.1 Conditions of Cores and Gas Hydrate Stability

After the hydrate core arrives at the laboratory, the first task is to assess the conditions of the core. Temperature and pressure records should be examined, and cores should be visually inspected (as at the rig site) to characterize and estimate the presence and amount of gas hydrate dissociation. Since the core samples containing gas hydrates may be shipped to core analysis laboratories in pressurized vessels, the pressure of each vessel must be checked and the dissociating gas should be collected. The analyzed gas composition will indicate the amount and type of gas hydrate dissociated.

In recent years, several groups have developed (or are trying to develop) methods to measure the gas hydrate stability in porous media, in a controlled manner (see, for example, Sloan, 2002, Westport Technology Center, 2002; Kono et al, 2002; Makogon,

2002; Turner and Sloan, 2002: Zhang et al, 2002; Zhang and Smith, 2002; Jones and Holditch, 2002; Paull et al, 2002; Zuidberg et al, 1998). Following Wright et al (1999), gas hydrate testing can be conducted in two stages. Stage 1 involves the regrowth of methane hydrate in sediments with known physical properties and pore-water salinities. Stage 2 involves the determination of pressure-temperature thresholds for methane hydrate stability in sediments, under controlled dissociation, between 32 ^{o}F and 54 ^{o}F. For low salinity sand, no discernible shift can be apparent in the P-T equilibrium thresholds. In the Mallik 2L-38 well analysis, tests on saline sands indicate a substantial but relatively uniform shift in P-T stability thresholds as pore water salinity increases. Pore water salinity and grain size characteristics of host sediments should be investigated, primarily because they are considered to have significant influence on natural gas hydrate occurrences in geological settings, including shifts in P-T stability thresholds, and imposing limits on the degree of pore occupancy by gas hydrate.

9.2 Chemical and Physical Properties of Gas Hydrates/Sediments

The important analysis of gas hydrate cores to be conducted include: crystal structure of the gas hydrate, molar ratio of water to guest gas molecules occupation in lattice sites, nuclear magnetic resonance (NMR), Raman spectroscopy, X-ray computerized tomography (CT) scanning, Scanning Electron Microscopy (SEM), inorganic and organic chemistry, gas hydrate kinetics, physical properties, and dissociation tests. These analyses provide information on the physical and chemical properties of gas hydrate formation and dissociation, and calculation of the amount of gas trapped within gas hydrate deposits. They also allow the comparison with values obtained from synthetic gas hydrate previously reported in the literature. The important tests to be conducted are described below and in Section 7.

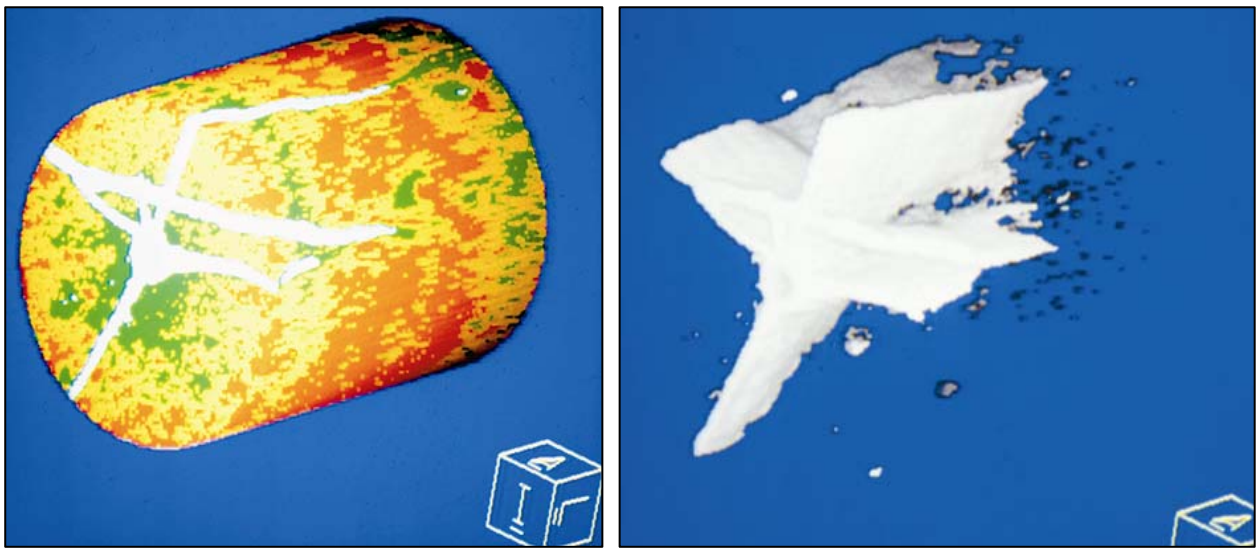
9.3 X-Ray Computerized Tomography (CT) Scanning

The X-Ray CT scan can be an important technique to characterize the gas hydrate bearing core samples, the presence of large mineral grains and some of the matrix characteristics and heterogeneity. The CT scanner is an important non-destructive technique for identifying occurrences of gas hydrate within sediments and their relationship to surrounding host sediments (Uchida et al, 1997, Freifeld et al, 2002, Westport Technology Center). This equipment was designed originally for medical use on human subjects and has been modified for observation of sediments/rock samples. In this method the images can be collected relatively rapidly with almost no gas hydrate dissociation. The measured CT values depend mainly on the x-ray absorption coefficient of the substance scanned, and are related to the bulk density.

The analysis of the Leg 164 samples shows that CT density values of methane hydrate range from –250 to –100, whereas those of pure water, pure water ice and dry ice are 0, -65 and 400, respectively. The CT values of sediment grains (minerals) usually exceed 1000, while common gases diminish to –1000, reflecting their densities.

The CT scan evaluates damaged zones, recovery and bedding plane dip. Invasion of drilling fluids may also be determined. A scout view (standard radiograph view) and a 90° scout-view should be taken from each 3' core segment. Nine slices 2mm thick should be obtained from each 3' tube. The locations should be picked once the scout view is obtained. The core should have dry ice packed around them while on the x-ray table. The core markings should be placed upward so that future orientations can be determined. More detailed procedures can be provided once the CT scan provider is determined. Figure 9.3.1 shows examples of CT scans showing a fractured core on the left and 3-D image of the fracture on the right.

Figure 9.3.1. CT Scanning- Core quality and data evaluation



9.4 Raman Spectroscopy

Raman spectroscopy can be used to detect the presence of hydrate crystals and to determine the structure of gas hydrate present at the hydrate stability boundary. Raman spectroscopy can also be used to conduct hydrate phase equilibrium measurements, with simultaneous detection of the hydrate structure. A hydrate Raman spectrum is used to detect the dissociation of hydrate in a regular phase equilibrium laboratory experiment. This experiment is non-intrusive and has the advantage to measuring both the hydrate point data and hydrate structure, simultaneously (Jager and Sloan, 2002).

Analysis of Mallik 2L-38 well (Uchida et al, 1999) shows that the following procedure can be adopted for future core analysis. This experiment is equipped with a dispersed monochromator system. Spectra are recorded using a photomultiplier tube detector system. The excitation system can be an argon-ion laser. A computer system provides control of data acquisition for the spectrometer system. Measurement can be performed in the frequency range 2800 to 3000 cm^{-1} to measure precisely the guest molecule

vibrations within the gas hydrate. Spectra can be collected with a 0.5 cm^{-1} scanning step and 5 second per step integration. The peaks of the Raman spectrum identify the gas forming the gas hydrate and indicate the purity of the gas, such as methane. Raman spectrum signal can also estimate the hydrate number of the samples.

The analysis of two samples, containing gas hydrates that occurred in intergranular pores in fine grained and granular sand, were performed by placing them in a specially designed cryostat. Temperature was controlled by liquid nitrogen flow to maintain a constant temperature ~ -58 ^{o}F. The magnification was 1000X with a 40X objective lens and diameter of the incident laser beam was 1 μm. This magnification is good to measure the size of gas hydrate or ice crystals within intergranular pores in the sediment. Raman spectra gave two peaks at 2904 and 2915 cm^{-1}. These peaks indicated that the specimen was almost pure methane gas having sI structure. This result corresponds to synthetic methane gas hydrate result and agrees well with data for natural gas hydrate obtained from ODP Leg 164.

9.5 NMR Spectroscopy

This is a physical method to characterize materials and to measure the gas hydrate structure. NMR spectroscopy and dielectric constant measurements provide evidence about the motion of water molecules in crystal structure, along with hydrate number and kinetics of formation of various structures. The chemical shift measures the extent to which the magnetic nucleus is shielded by surrounding electrons from an external magnetic field. This parameter is sensitive to the nature of gas hydrate cage.

NMR measurements are generally done with small plugs of sample size in the range of 1-1.5” diameter. Therefore, care should be taken so that the integrity of the samples is not destroyed.

There are two main techniques for the solid state: cross polarization and magic angle spinning techniques. Both spectra give peaks, which can be identified representing the gas molecule (for example, methane, occupying the small and large cages of the gas hydrate structure (Uchida et. al, 1999, Ripmeester and Ratcliffe, 1988)). The hydrate proton NMR analysis suggests that the first order contribution to motion is due to re-orientation of water molecules in the structure. The second order contribution is due to translational diffusion at the low temperatures, in which molecular motion is frozen so that hydrate lattices become rigid (< 50 K = -370 ^{o}F). This also offers a distinction between ice and water. Analyses show that water molecules diffuse two orders of magnitude slower in hydrates than in ice. Ice water molecules diffuse at nearly an order of magnitude faster than they re-orient about a fixed position in the crystal structure. In contrast, hydrate water molecules re-orient 20 times faster than they diffuse.

A brief guideline for this test is provided here based on the Mallik 2L-38 well sample test. A NMR spectrometer equipped with a probe for measuring solid substances was used for ^{13}C measurement. The sediment core sample was first crushed in liquid nitrogen and then pure gas hydrate particles were separated from crushed mineral-grain

clasts. The collected gas hydrate particles were packed tightly into a zirconia rotor (8mm in diameter and 10 mm long) and placed in the probe. The rotor was cooled to ~94 ^{o}F and driven at 3000 Hz by dry nitrogen gas. Signals were accumulated 4000 times with cross polarization/magic angle spinning (CP/MAS) technique, and 2000 times with MAS and high power decoupling for a total of 7 hours of experiment time. Two peaks of mass spectra were identified at about ~3 and ~7 ppm, indicating methane molecules occupying the small and large cages of the gas hydrate structure, respectively. Since these general intensity distribution data are consistent with those observed previously for sI gas hydrate (Ripmeester and Ratcliffe, 1988; Uchida et. al, 1997), this procedure is applicable for future NMR analyses.

9.6 Thermal Conductivity

Thermal conductivity is related to the complex mass and heat transfer processes associated with hydrate dissociation in a porous hydrate system. For example, actual data for hydrate/sand system are very sparse. Thermal conductivity depends not only on the intrinsic conductivity of the individual phases, but also on the thermal resistances across grain contacts (properties that depend on the quality, areas and geometry of such contacts). When gas hydrate dissociation and advective transport occur, estimating heat transport properties, and the migration rate of phase boundaries, are challenging.

Thermal conductivity of gas hydrate bearing sand samples should be measured using a specially designed probe plate apparatus of small samples at high pressure. For example, the thermal conductivity of Mallik 2L-38 sample ranges between 1.0251 and 0.626 W/m.K at temperature between –22 ^{o}F to 41 ^{o}F. GHASTLI is a useful equipment to measure hydraulic conductivity, in addition to acoustic and tri-axial strength, at different stages of testing (Winters et al, 1999A).

Recently, Waite et al (2002) have used the needle probe method to measure the thermal conductivity in low porosity samples of ice, pure methane hydrate, and methane hydrate+sediment mixtures. They formed samples by radially compacting granular hydrate around an axially positioned thermal conductivity needle probe. At 14 ^{o}F, measured thermal conductivities of compacted granular ice Ih and pure methane hydrate are 2.12 and 0.46 W/m.K, respectively. At 5 ^{o}F, the thermal conductivity of a 32 vol% methane hydrate, 68 vol% quartz sand mixture was 1.15 W/m.K. Over the measurement range, -4 ^{o}F to 14 ^{o}F for ice Ih, and –22 ^{o}F to 23 ^{o}F for pure methane hydrate, the dependence of thermal conductivity on temperature was –10.5x10-3 W/m.K/^{o}C and –8.14x10^{-4} W/m.K/^{o}C, respectively. This negative temperature dependence might result from methane gas in unconnected, intergranular porosity persisting after compaction. These results are consistent with published results (Matsumoto et al, 2000) except that Ross et al (1982) found a positive dependence on temperature on tetrahydrofuran (THF) hydrate. In a later development, Freifeld et al (2002) have tried to estimate thermal conductivity of hydrate/sand system using CT scan and their results were consistent with those of Waite et al (2002).

9.7 Electrical Resistivity

A specially designed electrode can be used to measure electrical resistivity of small gas hydrate samples at high pressure. The resistivity values provide a check on whether the samples have similar resistivities to synthetic gas hydrate or pure water ice. In the case of Mallik 2L-38 study, the apparatus was cooled down to –22 ^{o}F before placing the sample into the ring electrode, and pressurized to 1450 psi for several hours (Yamada and Nakamura, 1997). The specimen range was 15 mm in diameter and 8 mm in length. Resistivity results did not have similar resistivity to synthetic methane hydrate or pure water ice, but they were equivalent to the average values for sandstones (3.58×10^{3} Ohm.m at 14 ^{o}F pressurized to 1450 psi by methane gas). Similar procedure can be adopted for future tests.

9.8 Acoustic Velocity

Acoustic velocity measurement can be made on gas hydrate bearing sand as a function of temperature, and similarity of their values with synthesized gas hydrate can be compared. Again, we follow the example of Mallik 2L-38 well test for a future guideline. The sample of 40x30x30 mm size was fitted into a transducer designed to measure acoustic velocity at high pressure. The apparatus was cooled down to –22 ^{o}F, and then the sample was pressurized to 725 psi for several hours before measurements were made. The measurement system utilizes a sonic wave with 28 kHz frequency. At a temperature of 21.2 ^{o}F, Vp=3110 m/s, as compared to the synthesized methane, 1810-4010 m/s pressurized to 725 psi by helium gas. At 23 ^{o}F, that value was 3394 m/s as compared to synthesized methane, 2890-4110 m/s. Acoustic velocity measurements are also described by Rack (2001).

9.9 Mechanical Properties

Stress-strain relationship of the hydrated samples with time should be determined. Lately, a set of equipment has been proposed to measure thermal conductivity, mechanical properties, acoustic properties and permeability of gas hydrate in well constrained porous material (Bonnefoy and Herri, 2002). The equipment consists of saturator (volume=1.35 l, pressure=5075 psi), reactor (total volume = 9 l, under 4060 psi), pump (under 350 bar, operating in a constant flow rate mode or constant discharge pressure mode, flow rate range is 1-10 ml/min), gas flow rate controller (orifice size corresponds to a Kv of 4×10^{-5}), cryostats (max. flow rate is 17 l/min, minimum cooling temperature is –4 ^{o}F or –31 ^{o}F), gas booster, pressure (up to 4350 psi), gas flow meter (flow rate up to 200 Ncm^{3}/min), and temperature. The reactor is designed to receive instruments for measuring mechanical, acoustic, and electrical properties. The data acquisition is made by commercial software on a personal computer.

Shear tests provide a direct measure of shear strength of soft sediments. These results are used for foundation design, to detect relic slides, and to assess present slope stability (Zuidberg et al, 1998).

9.10 Gas To Water Ratio

A number of hydrate dissociation tests should be performed to investigate the gas to water ratio and the hydration number of the gas hydrate. Tests should be conducted on core samples from gas hydrate bearing, fine to medium grained sand. Small fragments of gas hydrate bearing sand can be placed into a small pressure vessel of known volume and then immersed in hot water in order to dissociate the gas hydrate within the sand. The pressure and temperature response of the vessel should be monitored allowing calculation of gas to water ratios. For example, in the Mallik 2L-38 case, gas to water ratio ranges from 44 to 153 indicating the structure I hydrate, based on the bulk volume of dissociated water to be 3cc and an average porosity of 30%, yielding 1 cc of pore water. For comparison, the pore saturation of gas hydrate was estimated to be greater than 70% (Miyairi et al, 1999).

9.11 Dissociation Kinetics

Dissociation kinetics of gas hydrate must be understood to assess the risk of a sudden gas release during exploration or production. This is also important for evaluating the resource potential of natural gas hydrate occurrences. Normal drilling fluids are typically composed of various chemicals, such as salts and glycols, which reduce gas hydrate stability both within the formation and within core samples. For the Mallik 2L-38 well, lecithin was used as an additive to the drilling fluid to stabilize gas hydrate during drilling. Lecithin is phospholipid and has been reported as an effective drilling fluid additive that keeps gas hydrate stable (Schofield et al, 1997, see also Section 5). Here we describe briefly the method adopted in analyzing the Mallik 2L-38 well samples, which can be recommended for future tests.

A core sample from Mallik's well from 903 m depth was used for testing. The sample consisted of a gas hydrate bearing, medium grained sand, about 60 mm diameter and 100 mm long. The sample of 270 g was divided in to five specimens, each between 40 g and 70 g. Each specimen was packed in a vinyl bag and placed within a smaller container that was cooled to –4.3 ^{o}F, and pressurized to 725 psi by N2 gas in a freezer. Lecithin is an insoluble solid in water and therefore comes as a 60-65% solution in oil. Water was added to a small amount of the lecithin-oil solution and formed a suspension. 6wt% lecithin-water solution and a water based drilling fluid (Telnite, a KCl/ polymer system) were used during drilling of the gas hydrate bearing formations.

Equipment consists of a cylinder, whose volume can be set in the range 0 to 500 cc by moving a piston connected to an autoclave with a 500 cc volume. The pressure in the system is automatically kept constant during hydrate dissociation by the piston. The rate of dissociation is measured by gas volume withdrawn, as a function of time at a constant pressure. The autoclave and the cylinder were placed in a cooling bath and cooling fluid was circulated to keep the temperature constant. Drilling fluid was cooled in advance and was introduced in the vessel by a hand operated pump after each specimen was placed in the vessel, and pressurized by methane gas to 725 psi. A

uniform mixing was obtained by vigorously agitating the sample and fluid. The temperature was then raised to 33.5 ^{o}F where C1 hydrate is stable at 725 psi. After the temperature became stable, pressure was decreased to 362 psi to dissociate hydrate at the above temperature. During these experiments, the amount of gas released and rates of dissociation were monitored successively by measuring the changes in piston position.

9.12 Gas Hydrate and Sediment Test Laboratory Instrument (GHASTLI) Study

The USGS has developed the Gas Hydrate and Sediment Test Laboratory Instrument (GHASTLI) system (Winters et al, 2000). Self-preserved hydrate samples, restored hydrate samples, or synthetic hydrate samples, can be tested in GHASTLI. The major objectives of the GHASTLI research were to measure physical properties in laboratory (preserve natural gas hydrate in sediment, test at in-situ pressure and temperature, measure acoustic and strength properties, determine the amount of gas hydrate present, etc.), relate amount of hydrate to properties, and model acoustic behavior.

The instrument was used to test Mallik 2L-38 samples. Test measurements include acoustic velocity, shear strength, hydraulic conductivity, permeability of sediment containing gas hydrate, and amount of gas hydrate in the pore space. Test samples from the Mallik 2L-38 well were trimmed on site from 133 mm to approximately 70 mm to fit into the transportation vessels. The process took 45 minutes for one set of samples and 30-45 minutes for the second. At the end of the trimming process, a section of core from a nearby depth was immersed in a dish of water and dissociation was visible. This led to the conclusion that the trimmed samples still contained hydrates and that the hydrate samples were self-preserved. The vessels were pressurized with methane to approximately 120 psi. Methane samples were taken for isotopic analysis. The core samples were stored at 21 to 14 ^{o}F for the trip to the USGS Lab in Woods Hole, Massachusetts. The GHASTLI system handles core samples sizes of 70 mm in diameter and 130 mm long. Maximum confining pressure for the sample is 3626 psi. The confining liquid is silicone oil. The sample is surrounded by a flexible impermeable membrane. Acoustic transducers and fluid flow ports are incorporated in the end caps. The bottom end cap sits on an internal load cell. A cooling system surrounds the vessel. Electrical resistance measurements are recorded horizontally using eight discrete probes along the perimeter. Figure 9.12.1 presents the physical properties of Mallik 2L-38 and schematics of the GHASTLI system are shown in Figures 9.12.2 and 9.12.3. A more detailed description of GHASTLI can be found elsewhere in this document (Winters et al, 1999A; 2002).

Figure 9.12.1 Mallik 2L-38 Physical Properties

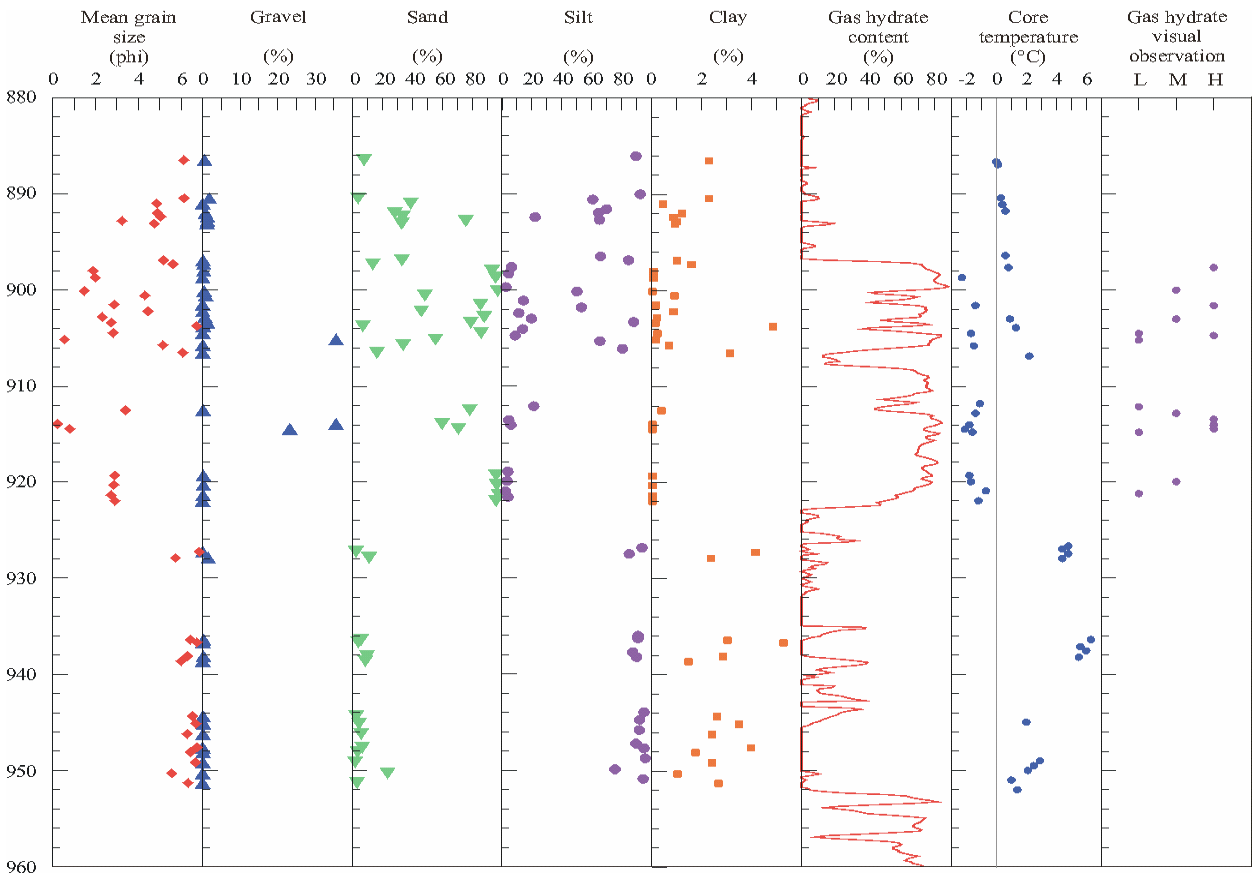

Mean grain size (phi)
Gravel (%)
Sand (%)
Silt (%)
Clay (%)
Gas hydrate content (%)
Core temperature (°C)
Gas hydrate visual observation
L M H
880
890
900
910
920
930
940
950
960

Figure 9.12.2 GHASTLI Simulation

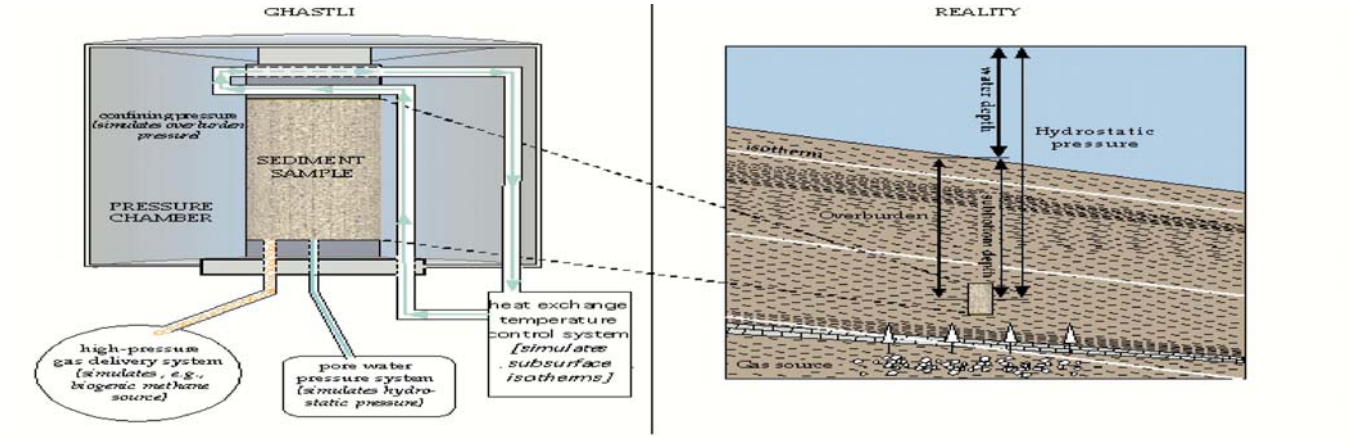
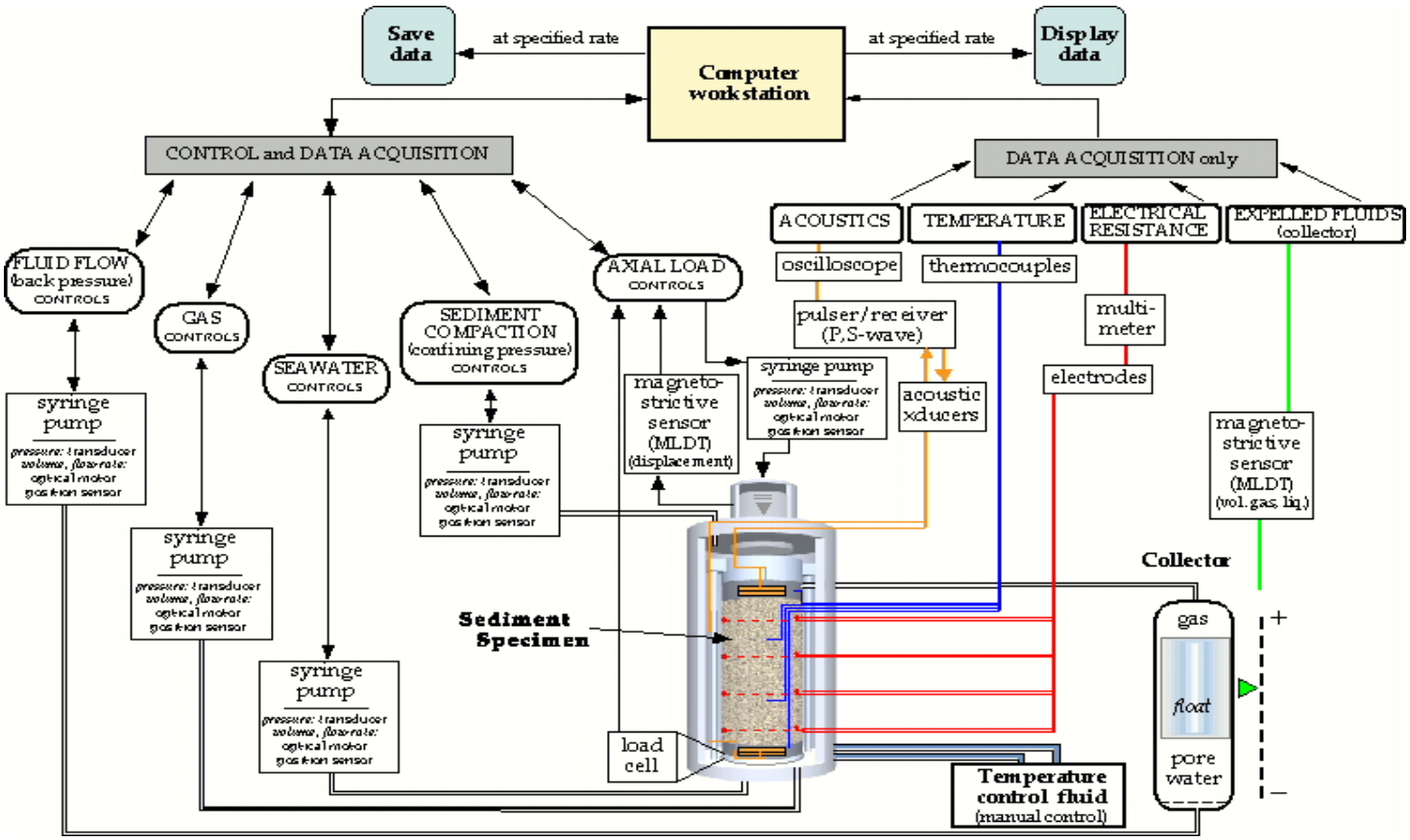


Figure 9.12.3 GHASTLI Sub-System



9.13 Physical Properties of Sediments- Porosity and Permeability

Porosity and air permeability measurements can be performed on sediments after the hydrate dissociates. The measurement of helium porosity is a common method used in the petroleum industry and is usually considered to be close to the absolute porosity value in a porous substance. In the Mallik 2L-38 well study, core specimens were subsampled and dried at 176 ^{o}F for a day before helium porosity and mercury porosimetry tests were performed. The pore size distribution of samples was determined by mercury injection porosimetry (Katsube et al, 1999). The mercury porosimeter measures the capillary pressure needed to force mercury into accessible pore spaces as well as the volume of mercury injected at each capillary pressure. Assuming that the pores are cylindrical in shape, the capillary pressure can be estimated for equivalent pore size, using the interfacial tension (about 0.48 N/m) and contact angle (about 139°) of the mercury. Pore size distribution can be derived from the capillary pressure data.

In this experiment the porosity and pore size distribution can be made for sand, silt and mud samples. The relationship between porosity, pore size, permeability and depths can be established. Helium and mercury porosities were found to be constant (about 30%) and mean and median radii were less than 1 μm. In both sandy and muddy sediments porosities and pore sizes gradually decrease with depth, due to diagenetic compaction of clastic sediment particles.

Permeability of unconsolidated sediments can be estimated using mercury capillary pressure data and are especially useful when direct measurements of permeability by fluids (such as air) cannot be obtained, due to difficulties caused by the shape of the unconsolidated samples. A relationship between recovery efficiency and mercury porosity, recovery efficiency and median pore radii, and recovery efficiency and permeability can be easily established. The pore radii can be calculated easily by Pr = 0.46 d, where Pr, is the pore radius and d is the mean grain size of the sediments (Uchida and Tada, 1992).

Pore volume is usually measured at several pressures up to the reservoir net overburden pressure. Measuring porosity and permeability under confining stress produces results that more accurately reflect in-situ values. Confining pressure should always proceed from the lowest value to the highest. The selected net overburden pressure is a value estimated for the well, based on the depth and pore pressure in the reservoir. Plug bulk volume is calculated from the sum of the gas expansion pore volume and the grain volume, measured in a helium pycnometer. Automated pore volume and permeability measurement is preferred because the duplication of procedures is more precise, and the results are more reproducible. It must be noted that exposure of core plugs to humidified laboratory air, which normally occurs with this equipment, must be eliminated by purging a plastic enclosure around the carousel with dry nitrogen gas. Plugs exposed to standard lab air for more than 30 minutes should be re-dried and re-weighed. Dry plugs should be stored in a desicator containing fresh

desiccant until the porosity and permeability measurements can be made. The equipment should be calibrated daily, prior to any measurements. Every tray of samples (about 10) should be run with both a porosity and a permeability check plug. Some labs check as often as every 5 samples. The porosity check plug should be the first sample in line so that if the correct value (±0.1%) is not obtained, the entire instrument can be re-calibrated.

Prior to automated pore volume and permeability measurements, the grain volumes should be measured, using a helium porosimeter that has been calibrated daily, using steel plugs of known volume. Three types of check samples (standard Berea sandstone, steel plugs and lead foil) should be run with each set of test samples. The instrument will be re-calibrated if any of these standards are not met. The grain volume data is used, along with the automated pore volume measurement, to calculate stressed porosity. Permeability to air is usually measured on all routine and vertical core plugs. The fine materials generated while cutting the plug should be cleaned from the plug faces with a brush before this measurement is made.

9.14 Pore Water Chemistry

When assessing engineering properties of gas hydrate bearing sediments, data are required on the effects of the porous media, and resident pore water on the pressure-temperature threshold for gas hydrate stability. Assessment of geo-mechanical properties such as strength and hydraulic conductivity are also critical. These properties can further establish the methane hydrate pressure-temperature stability conditions and porous media effect. The P-T threshold conditions predicted in laboratory testing should agree well with the observed base of the gas hydrate stability field, assessed on the basis of well-log interpretations.

9.14.1 Isotope Geochemistry of Dissociated Waters

Example of the Mallik 2L-38 well analyses provide guidelines to conduct these tests. Subsamples of dissociation water of Mallik's well were taken from frozen sediment from a core sample containing gas hydrate, and preserved within a pressure vessel. Each subsample was placed in a small flask in order to evaluate the isotopic equilibration with respect to Carbon Dioxide (CO_2) gas. The small flasks containing the subsamples were frozen in liquid nitrogen, evacuated, and then filled with CO_2 gas for Carbon isotopic equilibration reaction with the interstitial waters. The CO_2 flasks were then placed in an incubator at 77 ^{o}F for 10 to 15 hrs. A second subsample of 80-90 ml was squeezed from the sample using a Mannheim type hydraulic squeezer. Approximately 2 ml of interstitial water was obtained during the first hour of squeezing, and another 2 ml of interstitial water was obtained during the following 10 hrs of squeezing. An equilibrium CO_2 method was used to prepare the CO_2 gas samples from interstitial waters for oxygen isotope compositional determination (Matsuhisa and Matsumoto, 1985). The oxygen isotope ratio ($^{18}O/^{16}O$) of CO_2 gas was calculated using Finnigan Delta S Mass Spectrometers.

Results were obtained relative to the SMOW standard. Results showed that the $\delta^{18}O$ SMOW values of the gas hydrate dissociation waters were anomalously depleted in ^{18}O considering that the $\delta^{18}O$ SMOW of ocean waters are nearly 0% SMOW. This suggests the ^{18}O-deficient interstitial waters may have been significantly altered by ice-melting or, more likely, were derived from mixing of ocean waters and fresh waters.

9.14.2 Chloride Concentration of Pore Waters

The variation in chloride concentrations within the sediment cores is considered to be the most reliable parameter for determination of gas hydrate content in marine sediments (Paull et al, 1996). In the Mallik 2L-38 well, test pore waters were extracted from small subsamples of 50-100 cc, taken from 29 sediment core samples using a Mannheim type hydraulic squeezer. The volume of extracted water ranged between 0.3-5.2 ml, depending on the water content and size of core samples. These water samples were stored in vials immediately after extraction. Chloride concentration was determined by an ion-chromatograph IA-100. The amount of gas hydrate (pore saturation of hydrate) originally contained in the sediment cores was estimated. Pore saturation was calculated via:

$$GH\% = ((Cl_{bg} - Cl_{pw}) / Cl_{bg}) * 100$$

where GH% is the pore saturation (% volume) of the gas hydrate, Cl_{bg} is the chloride concentration of pristine pore water (baseline value of chloride assumed to be 518.75 mmol, gas hydrate free sediments), and Cl_{pw} is the measured chloride concentration of the samples. More detail of the procedure can be found elsewhere (Uchida et al, 1999). Uchida et al concluded that the chloride anomaly technique was a reliable and useful tool for estimating the gas hydrate content where baseline Cl values are known. In the case of freshwater to brackish water sediments, however, the lower chloride values were not necessarily indicative of gas hydrate presence.

9.15 Headspace Gas Chemistry

This provides information on the origin of methane in sediments. In this technique carbon isotope compositions of methane and hydrocarbons were analyzed using several gas samples. Hydrocarbon isotope compositions indicate any changes of hydrocarbon sources with depth. This analysis shows whether the methane is generated by microbial activities or migrated from thermally matured sediments. Pore water and gas geochemistry provides important insight into the geology of the Mallik reservoir as well as affecting the structure of in-situ gas hydrate. Gas kinetic studies are important to indicate that no thermogenic methane can be generated within the drilled section. Due to the high temperature requirements ($T > 32\ ^{o}F$) for its production, thermogenic gas must migrate from its source to the hydrate stability region. Thermogenic gas migration occurs via channels and faults, which are common to regions such as the GOM. Thermogenic, massive hydrates are associated with faults in fine-grained sediments rather than biogenic, dispersed hydrates in course grained rocks.

Molecular and isotopic compositions of recovered core and gases from core cuttings can establish the presence of a thermogenic methane component zone, microbial zone, or a combination of both.

9.16 Dean-Stark Analysis

The Dean-Stark method (API RP-40, 1998) is used to determine water saturation in a core sample. The proper procedure can be reviewed in that reference.

9.17 Extraction and Drying

Sample drying techniques are well described in API RP-40. Depending on the amount of clay in the sample, humidity drying may or may not be appropriate. For consolidated clean sandstone, conventional drying at 116 ºC, or vacuum drying at 90 ºC, are the preferred methods.

9.18 Bulk Volume

Bulk volume measurement techniques are explained in detail in API RP-40 (1998). Measurement techniques include Archimedes method, caliper, and grain volume plus pore volume.

9.19 Tracer Analysis

Tracer analysis procedures and possible lab choices are covered in Chapter 5 of Bloy's report (2001).

9.20 Photography

Gently clean the face of the ¼ or ½ slab and then photograph it in both white light and ultraviolet light. Depth markings should be readable on the core or Styrofoam insert. Other markings should include operator, well name, scale bar and color comparator. Photographing the core both wet and dry may assist in illustrating geological features. The sedimentologist describing the core may request close-ups of specific geological features. Repackage the ¼ or ½ slab and forward it for geologic description and prepare it for long-term storage.

9.21 Conventional Handling Methods for Poorly Consolidated Cores

Poorly consolidated core must be held in its original configuration until sampling is complete. This can be done by injecting materials such as epoxy or Plaster of Paris into the annulus, between the inner barrel and the core. However, the preferred approach is freezing the core with dry ice. The following sections assume the core is frozen. Note that freezing boxes, insulated chests, dry ice, insulated gloves, etc. must be added to the rigsite equipment lists. The procedures for handling conventional oilfield unconsolidated core are found elsewhere (API RP-40 (1998), Bloys (2001)).

10. CORE STORAGE

Core storage is an ongoing topic of discussion and research. Some samples show increased levels of dissociation if stored under nitrogen for a length of time after they have been subsequently warmed. If transportation is not an issue, the samples can be stored in methane or the dissociated gas can be reused. A guideline to preserve and store the gas hydrate samples for testing is given in Fig. 10.1. Further research will lead to guidelines on short and long-term storage to properly preserve the samples in the original condition.

There are three basic considerations for preservation and storage of gas hydrate cores: temperature, pressure, and type of gas to pressurize the sample.

10.1 Storage Temperature

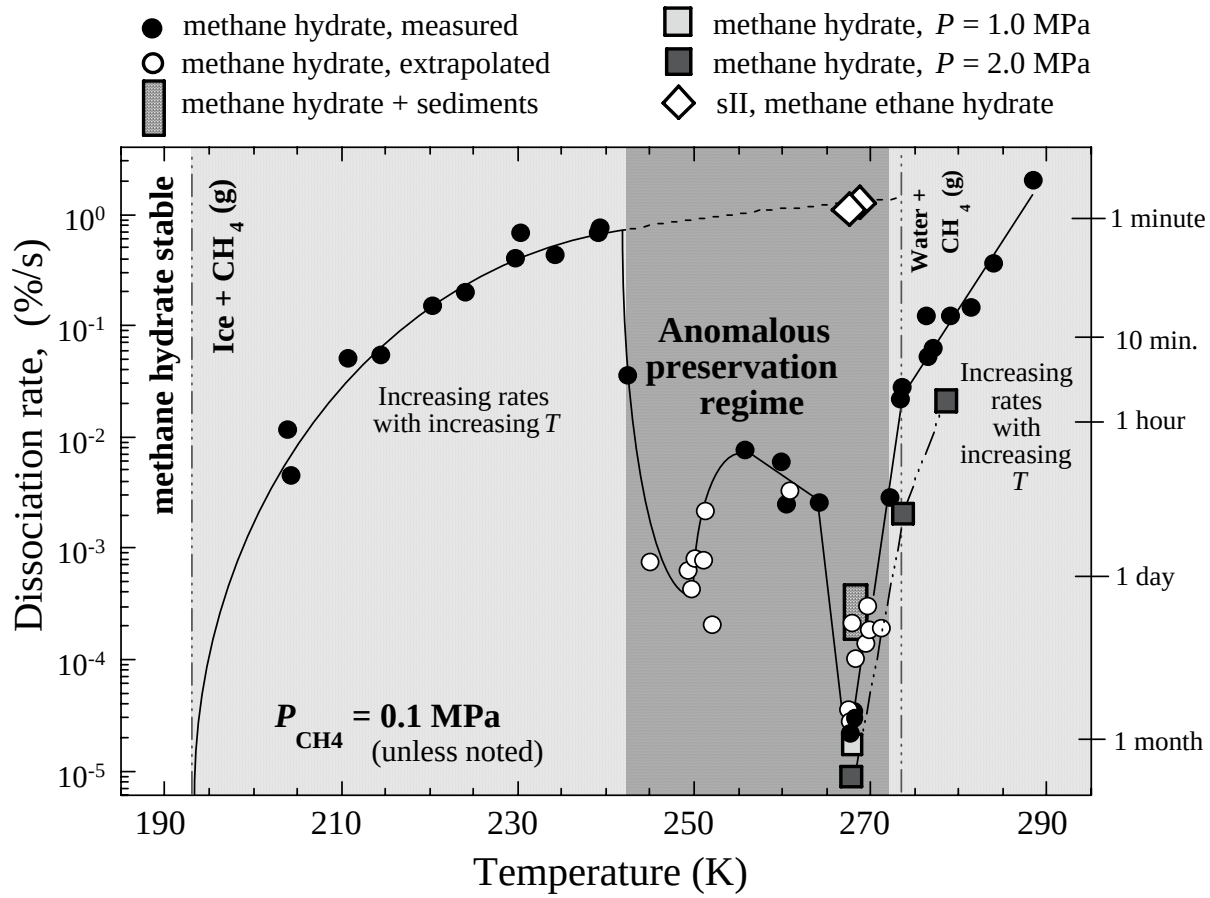
Past experience shows that core samples can be stored in liquid nitrogen, dry ice, and sub-freezing conditions.

The storage in liquid nitrogen involves wet storage, which was used by NRC Ottawa for many years, and dry storage, which is mandatory for air transport (for shipping small quantity by air, however, water vapor contamination issues are involved). The procedure is acceptable for tests performed at liquid nitrogen temperatures but accelerates dissociation if warmed.

The dry ice storage has been used successfully during Mallik 5L-38 to ship samples to Japan.

Kirby et al. conducted dissociation tests at varying initial pressures and temperatures, and measured dissociation rates as a function of temperature. They noted that the sub-freezing temperatures at about 25-14 ^{o}F appear to be optimum for cores that have been previously frozen (Kirby et al. 2003). Figure 10.1.1 shows the results of that series of tests.

Figure 10.1.1 Results of Dissociation Rate vs. Temperature



10.2 Gas Pressure

Atmospheric pressure is acceptable if stored in liquid nitrogen. Cores should self-preserve for days if kept frozen and sealed to prevent nitrogen contamination. The ideal pressure/temperature used should be below the stability threshold. Above the stability threshold for storage temperature there is potential to make hydrate even in frozen cores and to bring samples back to in-situ condition.

10.3 Gas Type

Three types of gases may be considered: a) non-hydrate former, which may induce dissociation from partial pressure effects, b) hydrate former such as methane, which can reduce dissociation but may cause additional hydrate formation depending on the hydrate forming conditions and, c) hydrate former, other than methane, which may be complicated.

10.4 Short Term Preservation

The best method for short-term preservation is at low to medium pressures, formation temperature, and with a suitable gas composition closely matching the hydrate composition, as the means of pressure creation. An adequate vessel of appropriate dimensions must be constructed to handle the conditions and to avoid excess dead volumes, which will reduce volume of gas needed to generate pressure.

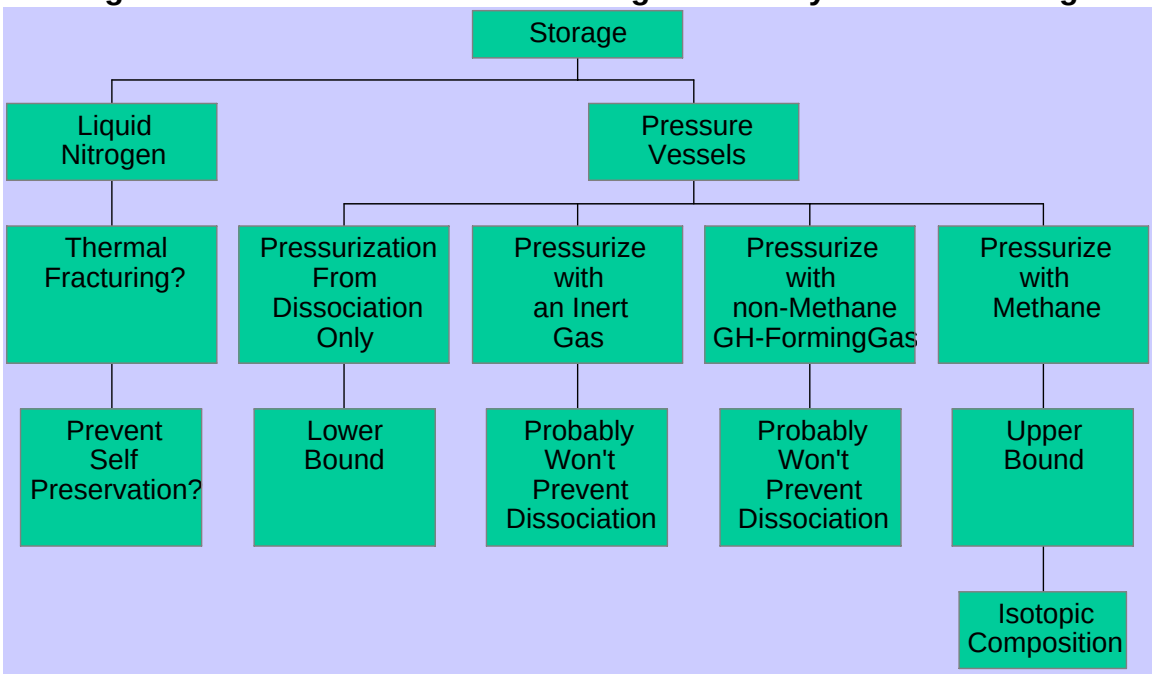
10.5 Long Term Preservation

Long term preservation of hydrate is currently done using liquid nitrogen and pressurized methods. The hydrate is preserved although nitrogen does diffuse into the core sample and change its condition. However, this may not interfere with the preserved gas hydrates.

10.6 Depressurization

Depressurized samples can be kept frozen near 0-10 ^{o}F to maintain sample integrity, but not hydrate integrity. However, hydrate conditions (T-P) can be monitored very well to verify whether there is any dissociation of gas hydrate.

Figure 10.6.1 Preservation and Storage of Gas Hydrate for Testing



10.7 ODP Experience on Leg 204

During ODP Leg 204 coring operations, a number of cores were selected for post-cruise preservation. The cores were pressure cores taken by the PCS, depressurized at the rig site, and quickly transferred into a pressure vessel. Approximately 50 meters of core were stored in pressure vessels, using methane as the carrier gas. Another 35 meters of core were preserved, using liquid nitrogen cryofreezers. Figure 10.7.1 shows the pressure vessels containing preserved hydrate core.

Figure 10.7.1 Pressure Vessels for Long Term Storage

11. SUMMARY/RECOMMENDATION

In this manual an overview of the existing information on Gas Hydrate Coring, Handling and Analysis is provided. The specific target involved coring sediments with hydrates in Alaska, the GOM and from an ODP drillship. The document describes coring sediments with hydrates, technology used in the coring, core handling, preservation and analysis at rigsite, transportation of the core to the destination laboratory analysis, analysis of the core, and the long term preservation of the core. A brief account of the gas hydrates in general, and their characteristics in sediments in particular, is presented to acquaint the reader with different aspects of gas hydrate formation and dissociation with/without sediments. The major sources of this review are books/monographs and published articles and reports in this field (see, for example, Sloan, 1998; Dallimore et al, 1999; Rack, 2001; Bloys, 2001, Westport Core Handling Manual, ChevronTexaco JIP Workshop, 2002, Proceedings of Yokohama Conference on Gas Hydrates, 2002, Westport/Maurer/Anadarko Workshop, 2002). Several other references contained in the above reports, along with the recent published articles in journals and private communications, were also reviewed.

Many questions are still to be answered. For example, maintaining the core conditions, use of conventional and pressure-temperature coring equipment, estimation of gas hydrate present in the core, laboratory analysis (from rigsite to laboratory) for both efficiency and cost effectiveness. This is particularly important in unconsolidated cores in the Gulf of Mexico, which present multiple unsolved challenges.

The properties to be investigated in the laboratory frame include the physical properties of sediments and hydrates: grain size, porosity, permeability, water content, pore-water salinity, grain density, bulk density, pore water, gas geochemistry, gas kinetics, molecular and isotopic compositions of recovered core and cutting gases, character and physical properties of gas hydrates and gas hydrate dissociation, NMR and CT Scan analyses, gas hydrate stability, geomechanical properties such as strength, resistivity, hydraulic conductivity, and acoustic properties. These are important for drilling operations, as well as for developing and testing models for future applications. An overview of physical property measurements performed on sediment containing gas hydrate is presented in Winters (1999B).

Based on the literature surveyed during the course of writing this report, the following recommendations can be made:

- For arctic environment, conventional or mining wireline coring, returns the largest diameter, longest cores. The PTCS can also be used if conventional rotary drilling equipment is used. However, use of the PTCS is restricted to 3 m long cores. Therefore, the conventional wireline systems are the preferred tools.
- For offshore environments, ODP has the best overall package currently available. The integration of coring and onsite analysis cannot be matched. Unfortunately, the small size (length and diameter) of the pressure cores, the limited success in unconsolidated sediments, and the lack of industrial targeted or goal oriented operations are of great concern for Gulf of Mexico applications. The PTCS can be used if the drillship is equipped with a fully functional mobile laboratory.

- The use of hydrate promoter in the drilling fluid assists in preventing dissociation of hydrates.
- Chilled drilling fluid with hydrate promoter is recommended for better hole stability and hydrate preservation.
- Freezing and maintaining samples at conditions at (or close to) that of the capture zone, is preferred to maintain hydrate equilibrium.
- Onsite testing capability is essential for hydrate analysis. The testing needs to be more focused on well log calibration (acoustic, mechanical, resistivity, and NMR measurements), hydrate dissociation properties, and hydrate productivity testing.
- Further research is necessary to verify the validity of self-preserved samples compared to fully preserved samples.
- Testing with whole core sections is recommended, due to possible hydrate quality problems during plugging.
- Sample preservation by use of re-pressurization with methane or formation gas, is appropriate.
- Offsite laboratory testing needs verification of consistent measurements in comparison with onsite measurements. Re-creation and dissociation in the laboratory of naturally occurring hydrates is a topic for further research.
- Further research is needed for long term storage of hydrate.
- Hydrate bearing core samples must be captured and maintained as close to pristine conditions as possible.
- Samples for CT scanning should be shipped in aluminum shipping containers to prevent unnecessary transfer, and possible further degradation, of samples at the laboratory.
- Air transportation is suitable for dry ice or liquid nitrogen shipping containers or when non-flammable gas is used for pressurization.
- The ground transportation for custom vessels and small vessels must have the current DOT certification.
- The storage of hydrate cores in liquid nitrogen (wet storage) was used by NRC Ottawa for many years. Dry storage is mandatory for air transport.
- The dry ice storage was used successfully during Mallik 5L-38 to ship samples to Japan.
- For previously frozen cores, the sub-freezing cores at 25-14 ^{o}F appear optimum.
- Atmospheric pressure is acceptable if core is stored in liquid nitrogen.
- For storage, two types of gases may be considered: a) non-hydrate former, which may induce dissociation from partial pressure effects, and b) hydrate former, which can reduce dissociation but may cause additional hydrate formation.
- Assemble and charge pressure vessels at simulated field conditions prior to arrival in the field.

The development of this manual will be an ongoing process. Data, experience and opinions from others will be requested and incorporated in the manual, as available and appropriate, during the course of this work.

ACKNOWLEDGEMENTS

We would like to acknowledge the support of DOE through the Project. We are grateful to John Rogers (DOE), Frank Rack (JOI), Ben Bloys (ChevronTexaco), Bill Winters (USGS), Siva Subramanian (ChevronTexaco), Steve Kirby (USGS), Tom Williams (Maurer), J. Kwan (Anadarko), R. Sigal (Anadarko), Laura Stern (USGS), Dendy Sloan (CSM), Tim Collett (USGS), and Lisa Avant (Westport) for their support and encouragement for accomplishing this task.

REFERENCES

Anderson, R., Biderkab, A.B., Tohidi, B. and Clennell, M. "Visual Observation of Gas Hydrate Formation in Glass Micromodels", Proc. 63rd EAGE Annual Conf., Amsterdam, 2001.

Baker, P.E. "Experiments on Hydrocarbon Gas Hydrates in Unconsolidated Sand", in I.R. Kaplan, ed., Natural Gases in Marine Sediments, *Plenum Press*, New York, 227, 1974.

Bloys, B.; "Low Invasion Coring: A Manual for Planning and Operation", ChevronTexaco E&P Technology Company, 2001.

Bonnefoy, O. and Herri, J.-M. "Formation and Dissociation of Methane Hydrates in Sediments", Proc. 4th Int. Conf., May 19-23, p.797-801, 2002.

Booth, J.S., Winters, W.J. and Mason, D.H. Capabilities of GHASTLI for Geo-Gas Hydrate Research. USGS Open File Rep. **94**-646, 1994.

Booth, J.S., Winters, W.J. and Dillon, W.P. "Apparatus Investigates Geological Aspects of Gas Hydrates", Oil and Gas Journal-Special, p.63-69, 1999.

Buffet, B.A. and Zatsepina, O. "Formation of Gas Hydrate from Dissolved Gas in Natural Porous Media", Marine Geology, **164**, p.69-77, 2000.

Capabilities of GHASTLI for Geo-Gas Hydrate Research. USGS Open File Rep 94-646, 1999.

Collett, T.S., Lewis, Rick and Uchida, T. "Growing Interest in Gas Hydrate", Oilfield Review, Page 42, Summer 2000.

Collett, T.S. "Natural Gas Hydrates of the Prudhoe Bay and Kuparuk River Area, North Slope, Alaska", AAPG Bulletin 77, no.5, 793-812, 1993.

Dallimore, S.R., Uchida, T. and Collett, T.S. Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Nortwest Territories, Canada", GSC Bulletin 544, p. 281-293, 1999.

Davidson, D. "Gas Hydrates as Clathrate Ices", Natural Gas Hydrates Properties, Occurrence and Recovery (ed. J. Cox), Butterworth, Woburn, MA, p. 1-16, 1983.

Fleischer, P., Orsi, T.H., Richardson, M.D. and Anderson, A.L. "Distribution of Free Gas in Marine Sediments: A Global Review", Geo-Marine Letters, **21**, p. 103-122, 2001.

Freifeld, B.M., Kneafsey, T.J., Tomutsa, L., Stern, L.A., and Kirby, S.H. “Use of Computed X-Ray Tomographic Data for Analyzing the Thermodynamics of a Dissociating Porous Sand/Hydrate Mixture”, On Gas Hydrates, Yokohama, May 19-23, p. 750-755, 2002.

Handa, Y. and Stupin, D. “Thermodynamic properties and Dissociation Characteristics of Methane and Propane Hydrates in 70A Silica Gel Pores”, J. Phys. Chem. 96, p.8599-8603, 1992.

Holder, G.D. “Gas Hydrates: Challenges for the Future”, edited by G. Holder, Annals New York Acad. Sci., 2000.

Howell, D.G., ed., The Future of Energy Gases, USGS Professional Paper 1570, p. 890, 1993.

Jager, M.D. and Sloan, E.D. “Structural Transition of Clathrate Hydrates Formed from Natural Gas”, On Gas Hydrates, Yokohama, May 19-23, p. 575-579, 2002.

Jones. E.H. and Holditch, S.a. “Characterizing Natural Gas Hydrates in the Deep Water Gulf of Mexico”, On Gas Hydrates, Yokohama, May 19-23, p.7-12, 2002.

Kono, H.O., Budhijanto, B., Narasimhan, S., Smith, D.H. and Song, F. “The Formation Rate of Methane Gas Hydrate Within Porous Sediments”, On Gas Hydrates, Yokohama, May 19-23, p. 543-546, 2002.

Kvenvolden, K.A. “A Primer on Gas Hydrate”, in D.G. Howell, ed., The Future of Energy Gases, USGS Professional Paper 1570, p. 279-291, p. 555-561, 1993.

Kvenvolden, K.A., Ginsburg, G.D. and Soloviev, V.A. “World-Wide Distribution of Subaquatic Gas Hydrates”, Geo-Marine Letters, 13, p. 32-40, 1993.

Laherrere, J.H.: “Gas Hydrates: Uncertain Resource Size Enigma”, Offshore Magazine, p. 140-141, 160-162, August, 1999.

Laherrere, J.H.: “Gas Hydrates: Data Shows Oceanic Methane Hydrate Resource Over-Estimated”, Offshore Magazine, p. 156-158, September, 1999.

Lowrie A. and Lerche, I. “Natural Gas Hydrates: Geologic Constituents from the Birth of Planet Earth to the Present”. OTC 14032, Houston, 2002.

Lowrie A., Max, M.D., Hamiter, R., Lerche, I. And Bagirov, E. “Hydrate Stability Zone Permanence along Dynamic Louisiana Offshore”, Trans. Gulf Coast Assoc. Soc., XLV11, p. 311-315, 1997.

Makogon, Y.F., Holditch, S.A., Holste, J.C. and Makogon, T.Y. “Aspects of Gas Hydrate Kinetics”, on Gas Hydrtaes, Yokohama, May 19-23, p. 531-536, 2002.

Matsuhisa, Y. and Matsumoto, R. “Oxygen Isotope Ratios of Interstitial Waters from The Nankai Trough and the Japan Trench, Leg 87”, in Initial Reports, Deep Sea Drilling Project **87**, (ed. H. Kagami, D.E. Karig and W.T. Coulboun, U.S. Government Office, Washington, 1985.

Matsumoto, R., Uchida, Ta., Waseda, A., Uchida, Ts., Takeya, S., Hirano, T., Yamada, K., Maeda, Y., and Okui, T. “Occurrence, Structure and Composition of Natural Gas Hydrate Recovered from the Blake Ridge, Northwest Atlantic”, Proc. Ocean Drilling Program, Sci. Results, (ed. C.K. Paull, R. Matsumoto, P.J. Wallace and W.P. Dillon), **164**, p. 13-25, 2000.

Max, M.D. and Lowrie, A. “Natural Gas Hydrates: Arctic and Nordic Sea Potential”, in T.O. Vorren, E. Bergsager, O.A. Dahl-Stamnes, B. Johansen, E. Lie and T.B. Lund, Arctic Geology and Petroleum Potential, Norwegian Petroleum Society, Spec. Pub. **2**, Elsevier, p. 27-53, 1992.

Max, M.D. and Lowrie, A. “Oceanic Methane Hydrates: A Frontier Gas Resource”, J. Petrol. Geol, **19**, p. 41-56, 1996.

Max, M.D. “Natural Gas Hydrate: in Oceanic and Permafrost Environments”, Kluwer Academic Publishers, Dordrecht, The Netherlands, p. 414, 2000.

Milkov, A. and Sassen, R. “Thickness of the Gas Hydrate Stability Zone, Gulf of Mexico Continental Slope”, *Marine and Petroleum Geology* **17**, 981-991, 2000.

Milkov, A. and Sassen, R. “Estimation of Gas Hydrate Resource, Northwestern Gulf of Mexico Continental Slope”, *Marine Geology* **179**, 71-83, 2001.

Miyairi, M., Akihisa, K., Uchida, T., Collett, T.S., and Dallimore, S.R.: “Well-log Interpretation of Gas Hydrate-Bearing Formations in the JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well”, GSC Bulletin **544**, p. 281-293, 1999.

OTC Proceedings, Offshore Technology Conference Held in Houston, Texas, May 6-9, 2002.

Ohara, T., Dallimore, S.R., and Fercho, E. “JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, N.W.T.: Overview of Field Operations”, Paper SPE 59795 Presented at the SPE/CERI Gas Technology Symposium, Calgary, Alberta, Canada, April 3-5, 2000.

Paull, C.K., Brewer, P.G., Ussler III, W., Peltzer, E.T., Rehder, G. and Clague, D. “Evaluation of Marine Slumping as a Mechanism to Transfer Methane from Seafloor Gas Hydrate Deposits into the Upper Ocean and Atmosphere”, On Gas Hydrates, Yokohama, May 19-23, p.31-35, 2002.

Paull, C.K., Matsumoto, R. and Wallace, P. “Gas Hydrate Sampling on the Blake Ridge and Carolina Rise”, Proc. Ocean Drilling Program, Initial Reports, ODP, College Station, Texas, **164**, p.623, 1996.

Prensky, S.E. “A Review of Gas Hydrates and Formation Evaluation of Hydrate Bearing Reservoirs”, Soc. Prof. Well Log Analysts, Paris, France, June 26-29, 1995.

Proceedings of the 4th International Conference on Gas Hydrates, Yokohama, Japan, Vols. **1 & 2**, May 19-23, 2002.

Rack, Frank. “Preliminary Evaluation of Existing Pressure/Temperature Coring Systems”. From In-Situ Sampling and Characterization of Naturally Occurring Marine Hydrate Using The D/V JOIDES Resolution, Joint Oceanographic Institutions, October, 2001.

Ripmeester, J.A. and Ratcliffe, C.I., “Low Temperature Cross Polarization/Magic Angle Spinning 13C NMR for Solid Methane Hydrates: Structure, Cage Occupancy and Hydration Number”, J. Phys. Chem., **92** p.337-339, 1988.

Ross, R.G. and Anderson, P. “Clathrate and Other Solid Phases in the Tetrahydrofuran-Water System: Thermal Conductivity and Heat Capacity Under Pressure”, Can. J. Chem., **60**, p. 881-892, 1982.

Sassen, R., Sweet, A.V., Milkov, A.V., DeFreitas, D.A., Kennicutt, M.C. and Roberts, H.H. “Stability of Thermogenic Gas Hydrate in the Gulf of Mexico: Constraints on Models of Climate Change”. In C.K. Paull and W.P. Dillon, Eds. Natural Gas Hydrates: Occurrence, Distribution and Dynamics. *AGU Monograph Series* **124**, 131-143, 2001.

Sassen, R., Joye, S., Sweet, S.T., DeFreitas, D.A., Milkov, A.V. and McDonald, I.R. “Thermogenic Gas Hydrates and Hydrocarbon Gases in Complex Chemosynthetic Communities, Gulf of Mexico Continental Slope”. *Organic Geochemistry* **30**, 485-497, 1999.

Shukla, K., Trenery, J., Hakimuddin, M. and Fleyfel, F. “A Novel Model of Gas Hydrate Control for Deep Water Drilling Operations”, SPE Meeting, Houston, 2000.

Trenery, J., Magri, N., Shukla, K., Fleyfel, F., Halal, A. and Yousif, M. “Gas Hydrate Control for Deep Water Drilling Operations”, Final Report, WTCI, October, 2000.

Takahashi , H., Yonezawa, T. and Takedomi, Y. "Exploration for Natural Hydrate in Nankai-Trough Wells Offshore Japan,", JAPEX./JNOC/METI,OTC, Houston, April 30 – May, 2001.

Trenery, J., Magri, N., Shukla, K., Fleyfel, F., Halal, A. and Yousif, M. “Gas Hydrate Control for Deep Water Drilling Operations”, 1st Quarterly Report, WTCI, May, 1999.

Sloan, E.D., “Clathrate Hydrates of Natural Gases”, 2nd Edn., Marcel Dekker, New York, 1998.

Sloan, E.D., “Hydrate Engineering”, SPE Monograph (edt. J.B. Bloys), V. **21**, Richardson, Texas, 2000.

Subramanian, S., Private Communication (2002).

Takahashi, H., Yonezawa, T. and Takedomi, Y.: “Exploration for Natural Hydrate in Nankai-Trough Wells Offshore Japan”, Paper OTC 13040 Presented at the 2001 Offshore Technology Conference, Houston, TX.

Turner, D. and Sloan, E.D. “Sediment Effect on Hydrate Equilibria”, Deepwater Geohazards Workshop, del Lago, Texas, April 3&4 2001.

Turner, D. and Sloan, E.D. “Hydrate Phase Equilibria Measurements and Predictions in Sediments”, On Gas Hydrates, Yokohama, May 19-23, p.327-330, 2002.

Uchida, T. and Tada, R. “Pore Properties of Sandstones-Part II. Application for Pore Size Distribution to Natural Sandstones”, J. Japanese Association of Petroleum Geologists, **57**, p.213-222, 1992

Uchida, T., Hailong, L., Tomaru, H., Dallimore, S., Matsumoto, R., Oda H., Delwiche, M. and Okada, S. “Japan’s Efforts to explore marine Gas Hydrates off Tokai at the Nankai Trough and Their Occurrences: Geological Overview”. Supplement to EOS, Transactions, American Geophysical Union 81, 22, WP50, 2000.

Uchida, T., Dallimore, S.R., Mikami, J., and Nixon, F.M.: “Occurrences and X-ray Computerized Tomography (CT) Observations of Natural Gas Hydrate, JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well”, GSC Bulletin 544, p. 197-204, 1999.

Uchida, T., Matsumoto, R., Waseda, A., Okui, T., Yamada, K., Uchida, T., Okada, S. and Takano, O. “Summary of Physicochemical Properties of Natural Gas Hydrate and Associated Gas-Hydrate-Bearing Sediments, JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well”, GSC Bulletin 544, p. 205-228, 1999.

Uchida, T., Ebinuma, T., and Ishizaki, T. “Dissociation Condition Measurements of Methane Hydrate in Confined Small Pores of Porous Glass”, J. Phys. Chem. B, Vol. **103**, p. 3659-3662, 1999.

Uchida, T., Mikami, J., Masuda, Y., and Satoh, T.: “Dissociation Properties of Natural Gas Hydrate from the JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well by X-ray Computerized Tomography (CT) Experiments”, GSC Bulletin **544**, p. 269-279, 1999.

Uchida, T., Matsumoto, R., Waseda, A., Okui, T., Yamada, K., Uchida, T., Okada, S., and Takano, O.: "Summary of Physiochemical Properties of Natural Gas Hydrate and Associated Gas-Hydrate-Bearing Sediments", GSC **544**, p. 205-228, 1999.

Uchida, T., Yamamoto, J., Okada, S., Waseda, A., Baba, K., Okatsu, K., Matsumoto, R., and Shipboard Scientific Party of ODP Leg 164. "Methane Hydrate in Deep Marine Sediments-X-ray CT and NMR Studies of ODP Leg 164 Hydrates", Journal of Geological Survey of Japan, **510**, p. 36-42, 1997.

Ussler III, W., Paull, C.K., McGill, P., Schroeder, D. and Ferrell, D., "Estimating in situ Sediments Gas Concentrations in ODP Boreholes by Continuously Monitoring Temperature During Core Recovery", On Gas Hydrates, Yokohama, May 19-23, 2002.

Waite, W.F., Pinkston, J. and Kirby, S.H. "Preliminary Laboratory Thermal Conductivity Measurements in Pure Methane Hydrate and Methane Hydrate-Sediment Mixtures: A Progree Report" On Gas Hydrates, Yokohama, May 19-23, p.728-733, 2002.

Westport Core Handling Manual, Westport Technology Center, Houston, Texas, 1995.

Westport Technology Center, DOE Project, Houston, Texas, 2002.

Westport/Maurer/Anadarko Workshop, Anadarko Building, The Woodlands, Texas, October 18, 2002.

Whitson, C.D. and Mcfadyen, M.K. "Drilling Deep Subsalt Wells in Deepwater Gulf of Mexico", JPT, June, p. 40-41, 2002.

Winters, W.J., Dillon, W.P. and Pecher, I.A: "GHASTLI – Determining Physical Properties of Sediment Containing Natural and Laboratory-Formed Gas Hydrate", in Natural Gas Hydrate in Oceanic and Permafrost Environments, ed. Michael D. Max, Kluwer Acad. Pub., Dordrecht, The Netherlands, p. 311-322, 2000.

Winters, W.J., Pecher, I.A., Booth, J.S., Mason, D.H., Relle, M.K. and Dillon, W.P.: "Properties of Samples containing Natural Gas Hydrate from the JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Determined Using Gas Hydrate and Sediment Test Laboratory Instrument (GHASTLI)", GSC Bulletin **544**, p. 241-250, 1999.

Winters, W.J., Dallimore, S.R., Collett, T.S., Katsube, T.J., Jenner, K.A., Cranston, R.E., Wright, J.F., Nixon, F.M., and Uchida, T.: Physical Properties of Sediments from the JAPEX/JNOC/GSC Maillik 2L-38 Gas Hydrate Research Well", GSC Bulletin **544**, p. 95-100, 1999.

Winters, W.J., Waite, W.F., Mason, D.H., Dillon, W.P. and Pecher, I.A. "Sediment Properties Associated With Gas Hydrate Formation", On Gas Hydrates, Yokohama, May 19-23, p.722-727, 2002.

Physical Properties of Sediments from the JAPEX/JNOC/GSC Maillik 2L-38 Gas Hydrate Research Well", GSC Bulletin **544**, p. 95-100, 1999.

Winters, W.J., Booth, J.S., Nielsen, R., Dillon, W.P. and Commeau, R.F. A Computer Controlled Gas Hydrate Sediment Formation and Triaxial Test System. Ann. N.Y. Acad. Sci., **715**, 490, 1994.

Yuan, J. and Edwards, R.N. "The Assessment of Marine Gas Hydrates Through Electrical Remote Sounding: Hydrate Without a BSR", Geophysical Research Letters **27**, no. 16, 2397, 2000.

Zhang, W., Wilder, J.W. and Smith, D.S. "Equilibrium Pressures and temperatures for Equilibria Involving Hydrate, Ice, and Free Gas in Porous Media", On Gas Hydrates, Yokohama, May 19-23, p.321-326, 2002.

Zhang, W. and Smith, D.S. "Constructing Thermodynamic Equations for Ice-Hydrate Equilibria in Porous Media", On Gas Hydrates, Yokohama, May 19-23, p.412-417, 2002.

Zuidberg, H., Baardman, B., Kobayashi, I. and Tsuzuki, M. "Geotechnical Techniques for Deep Water Coring and Testing Gas Hydrates", Methane Hydrates-Resources in the Near Future, JNOC-TRC, Japan, Oct. 22-23, 1998.

LIST OF ABBREVIATIONS

APC	Advanced Piston Coring
BHA	Bottom Hole Assembly
BSR	Bottom Simulating Reflector
C1	Methane
C5	Pentane
CSM	Colorado School of Mines
CT	Computerized Tomography
DOE	Department of Energy
DOT	Department of Transportation
^{O}F	Degree Fahrenheit (Temperature)
FPC	Fugro Pressure Corer
GHASTLI	Gas Hydrate and Sediment Test Laboratory Instrument
GOM	Gulf of Mexico
HRC	HYACE Rotary Corer
HYACE	Hydrate Autoclave Coring Equipment
JAPEX	Japan Petroleum Exploration Co.
JIP	Joint Industry Project
JNOC	Japan National Oil Corporation
m	Meter
N2	Nitrogen
NMR	Nuclear Magnetic Resonance
NRC	National Research Council (Canada)
ODP	Ocean Drilling Program
OTC	Offshore Technology Conference
PCS	Pressure Coring System
PTCS	Pressure-Temperature Coring System
PV	Pressure Vessel
QC/QA	Quality Control/Quality Assurance
RCB	Rotary Core Barrel
SCAL	Special Core Analysis Laboratory
THF	Tetra Hydro Furan
USGS	United States Geological Survey
Vp	Compressional Wave Speed
Vs	Shear Velocity
WHYP	Westport Gas Hydrate Prediction Program

APPENDICES

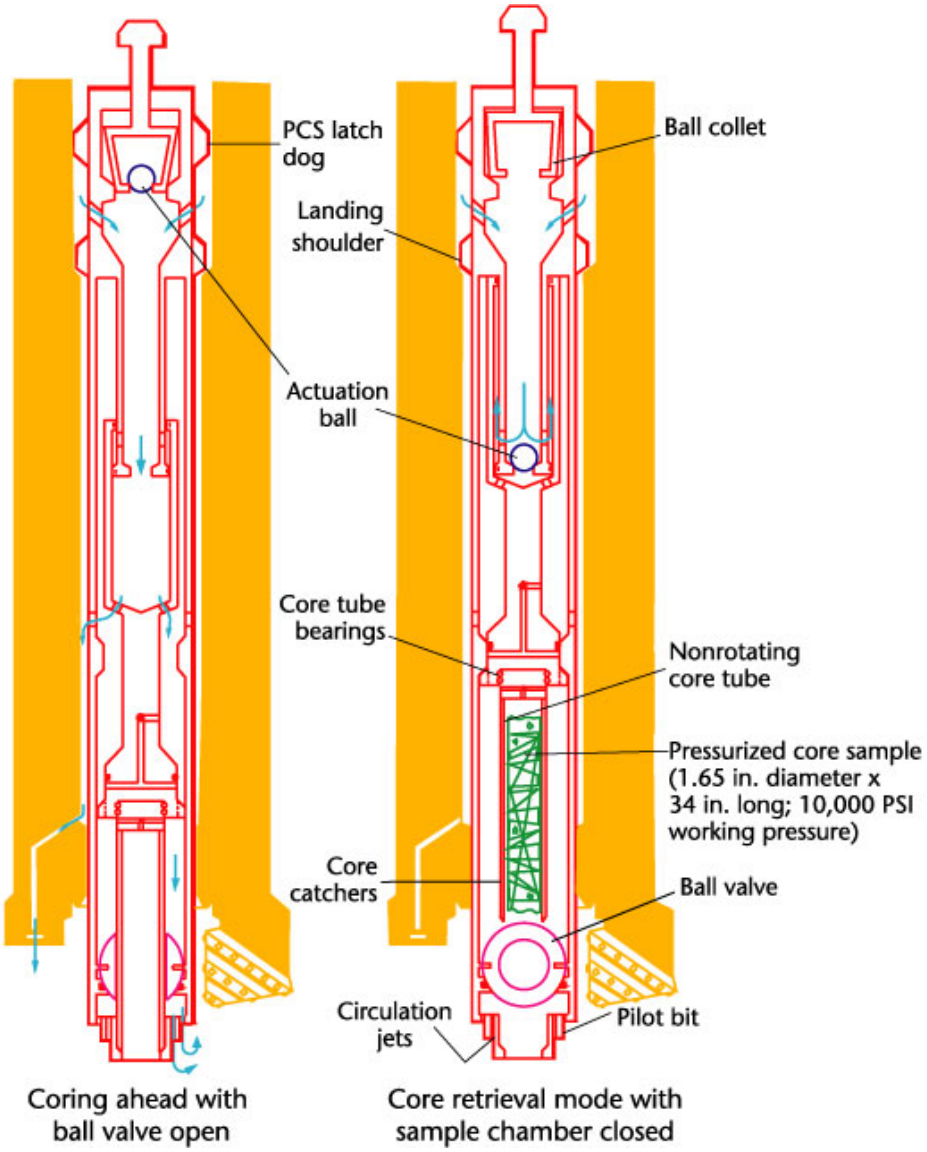
Here, we present only a brief account of the four types of coring tools used in the ODP system, as examples. The detailed discussion about the various ODP coring tools as well as coring tools used in other programs can be found in the Report of Rack (2001) and Bloys (2001). However, upon request from the reader the appendices discussed in the manual can be obtained on CDs from Westport Technology Center.

Appendix A. ODP Coring Equipment (PCS/APC/APCT/RCB/XCB/DVTT)

A.1 Pressure Core Sampler (PCS)

The PCS is capable of retrieving core samples from the ocean floor while maintaining in situ pressure up to 10000 psi. The PCS is free-fall deployable and wireline retrievable. A schematic of the PCS is presented in Fig.A.1 in the coring ahead mode with the ball valve open to accept core (left). After cutting the core (right), the wireline is picked up to release the ball, which redirects fluid to lift the core tube for core retrieval mode (with the core tube and core retracted inside the tool and the ball valve closed).

Figure A.1 Schematic Representation of PCS (Arrows Indicate Fluid Flow)



A.1.1 Tool Operations

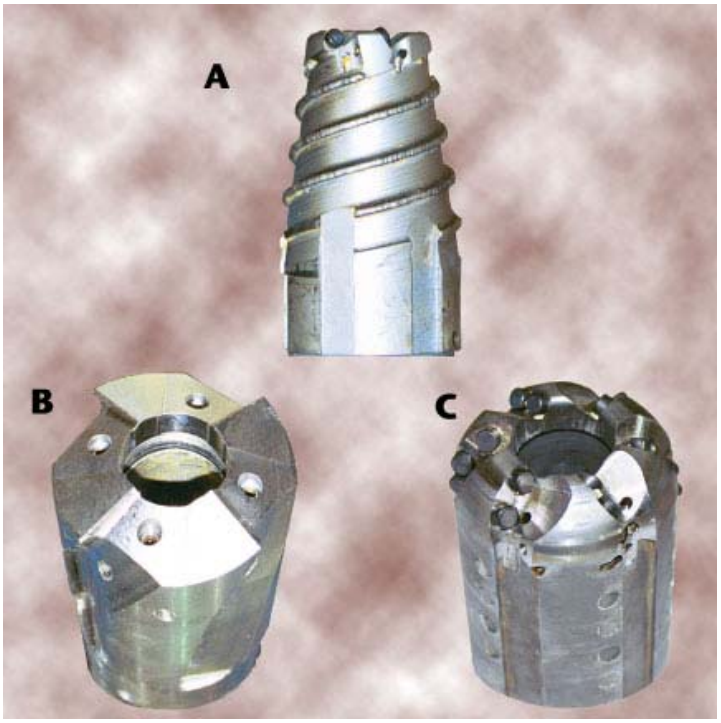
The PCS is free-fall deployable down the drill string for intermittent spot coring while using the Advanced Piston Corer/Extended Core Barrel (APC/XCB) bottomholr assembly (BHA). The PCS inner core barrel is latched in to the XCB rotary window sub and is rotated with the drill string while weight is applied to the bit. After cutting the core, a ball is released by wireline action to divert flow to a piston that pulls the core tube into the pressured core barrel and closes the ball valve. The core is then retrieved by wireline.

A.1.2 Design Features

- The PCS is compatible with the existing BHA for the APC and XCB coring systems.
- The PCS can be deployed during routine coring without a pipe trip
- The PCS latch dog locks into the APC/XCB latch window in BHA which transmits BHA rotation to PCS. A combination of low weight on bit, slow rotation, and low pump rate is required to core
- Fragile samples and sticky clays can be recovered with minimal hydraulic disturbance or contamination
- After the PCS sample is cut, the actuator hydraulically pulls the inner core barrel and core sample through a ball valve into the sample chamber and closes the ball valve, thereby sealing the sample chamber at in situ pressure
- The PCS core sample is trapped at in situ pressure behind a ball valve that closes by rotation to maintain its seal at both positive and negative pressure differentials
- A removable pressure chamber maintains the core sample at in situ pressure, provides for internal pressure monitoring, incorporates safety pressure release mechanisms, and offers two sampling ports for collecting gas and fluids
- Permits the pressure core sample chamber to be removed to a lab for further analysis
- The specifications, operating range and limitations of the PCS tool are described in Section 4.1 and in the report of Rack (2001)

Figure A2. PCS Coring Bits

There are three bits available for rotary coring with the PCS tool: RBI auger bit (**A**), Christiansen standard bit (**B**), and RBI PDC bit (**C**).



A.2 Advanced Piston Corer (APC)

The APC is crucial for high-resolution climate and paleoceanographic studies. The APC is hydraulically actuated piston corer designed to recover relatively undisturbed continuous 9.5 meter long oriented core samples from very soft to firm sediments that cannot be recovered well by rotary coring. A schematic of APC is presented in Figure A.2 before and after stroking out the inner core barrel to take a core. Pump pressure inside the drill string severs the shear pins and allows the inner core barrel to stroke out 9.5 m in 2-3 seconds with ~ 27000 lb of force.

Figure A.3 A Schematic Representation of APC

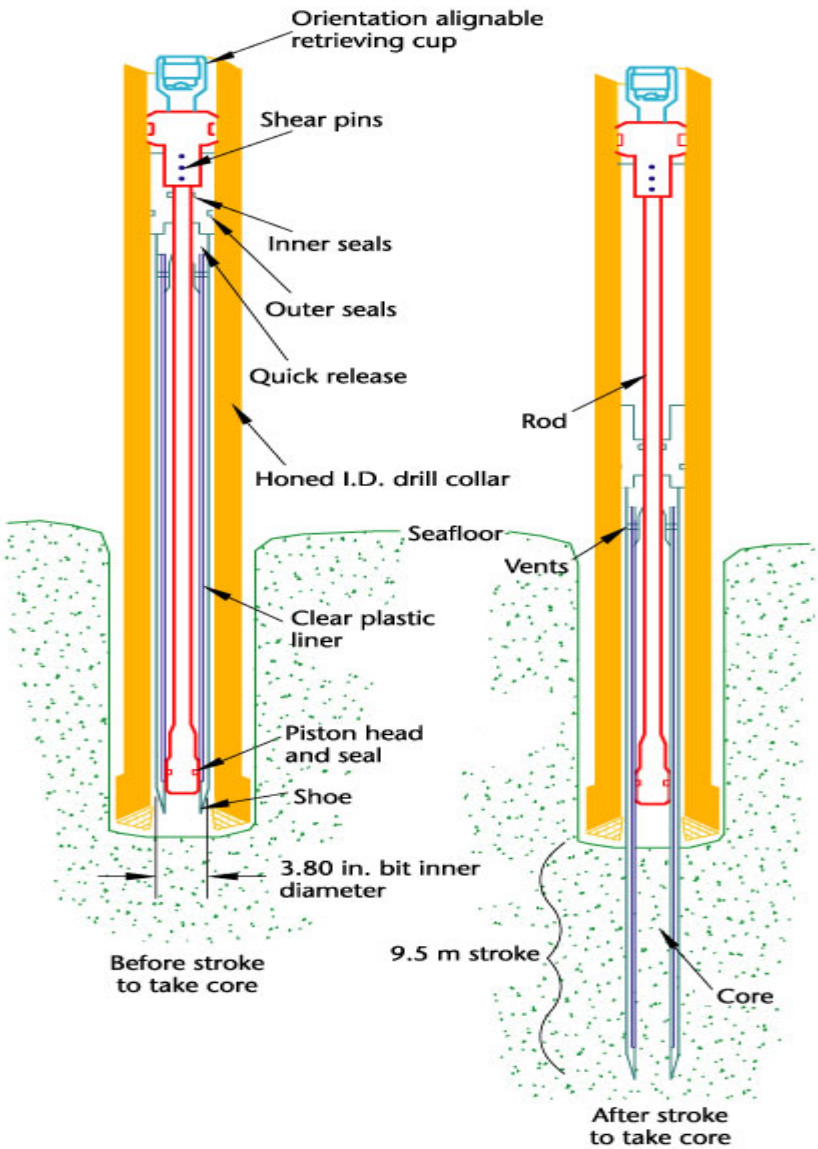
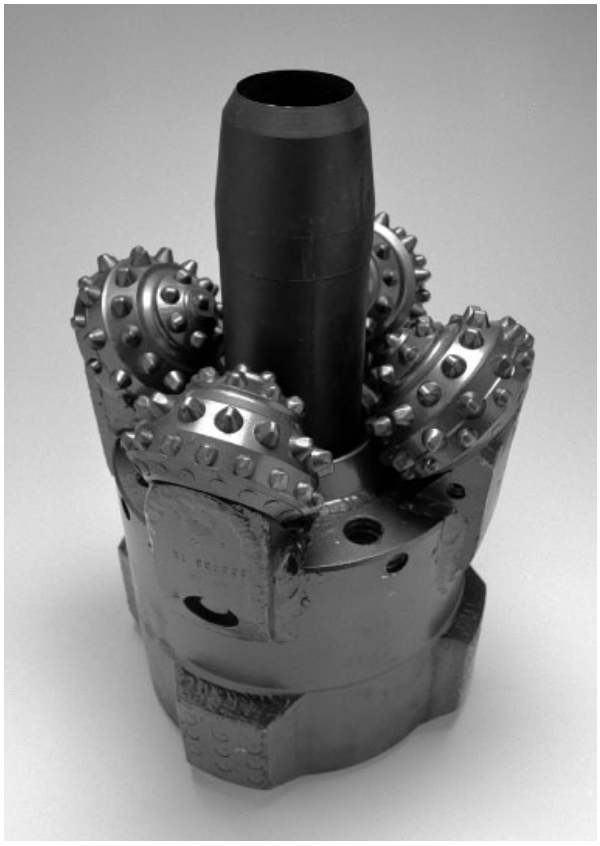


Figure A.4 APC Coring Bit



A.2.1 Tool Operations

The APC inner core barrel runs to bottom on the coring wireline. Pump pressure is applied to the drill pipe, which severs the shear pins and strokes the inner core barrel out 9.5 meter into the sediment. The inner core barrel containing the core is retrieved by wireline. A wireline packoff at the top of drill string permits rotation of the drill string and continued circulation while the core is retrieved. After core retrieval, the bit and bottom-hole assembly (BHA) are again advanced 9.5 m, repeating the process.

A.2.2 Design Features

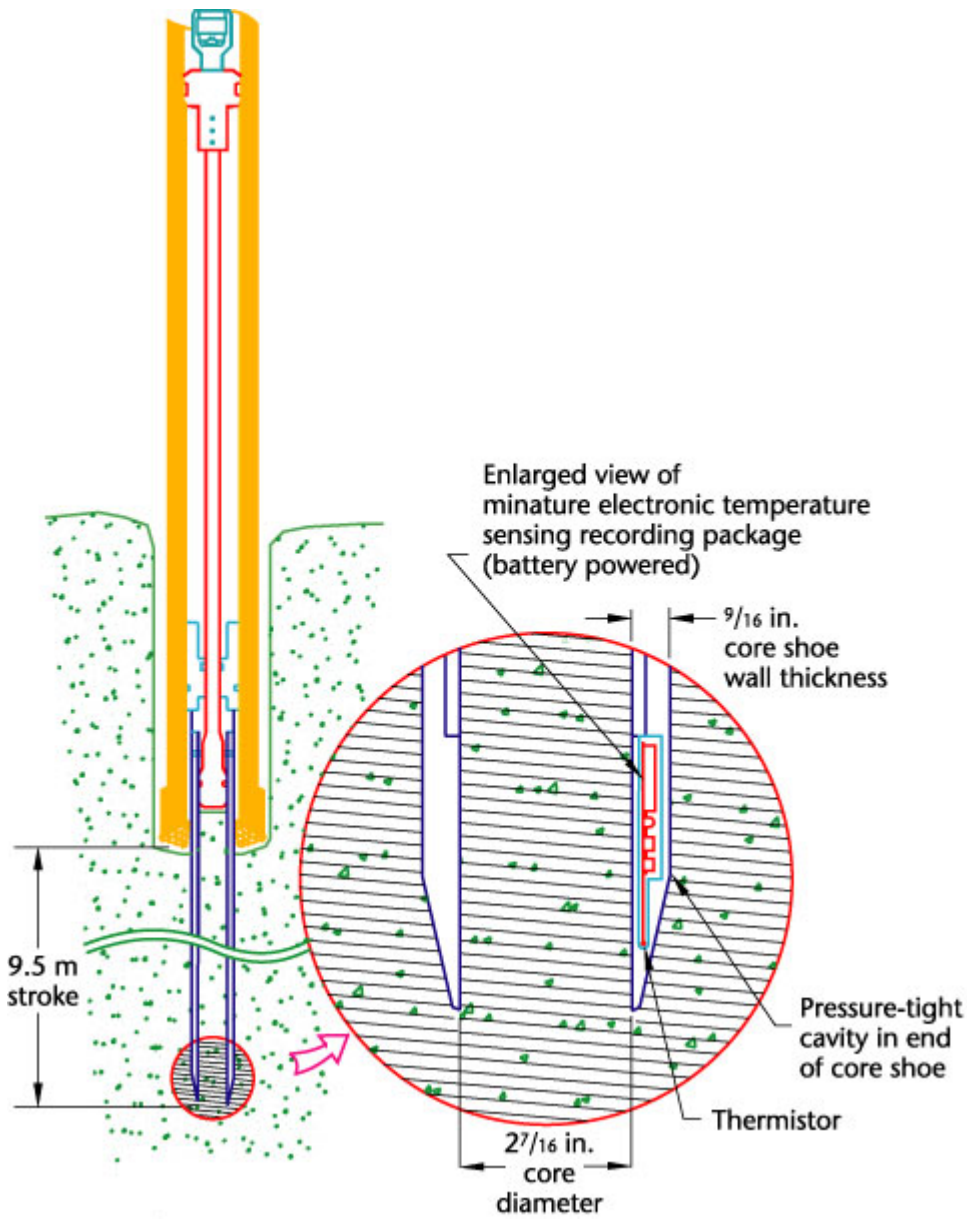
- The APC inner barrel is run in the same BHA as the Extended Core Barrel (XCB). Therefore, both tools can be used interchangeably depending on formation lithification
- The Motor Driven Core Barrel and Pressure Core Sampler are also compatable with APC/XCB/BHA
- The benefits are that tools are interchangeable and no time is spent for bit trips
- The APC inner core barrel is deployed and recovered using the coring wireline to avoid premature failure of the shear pins, which determine penetration force of the barrel into the sediment

- The APC allows rapid recovery of core with minimal nonproductive time
- The APC core can be oriented with respect to the Earth's magnetic pole by running a downhole orientation tool above the core barrel.
- A tensor electronic unit is used to provide more accurate orientation, improve dependability, and reduce maintenance.
- The APC allows recovery of oriented core for paleomagnetic studies
- The APC shoes have a pocket in which a thermistor unit can be run to record the in situ formation temperature after taking a core
- The APC provides in situ heat flow measurements
- The specifications, operating range and limitations of the APC tool are described in Section 4.1 and in the Report of Rack (2001)

A.3 Advanced Piston Corer Temperature (APCT)

The APCT tool is an instrumented version of the coring shoe in sediments that is run on the APC. It is deployed in soft sediments to obtain formation temperatures to determining the heat flow gradient and is essential in determining hydrocarbon maturity for pollution prevention purposes. A schematic of APCT is presented in Figure A.3.

Figure A.5 A Schematic Representation of APCT



A.3.1 Tool Operation

The APCT is deployed on an APC inner core barrel and provides a precise in situ temperature measurement while adding only 10 min to each core barrel. The tool is run starting at 30 m below seafloor and the run after every other core until four good readings are obtained. The shoe is hydraulically stroked 9.5 m into the sediment and remains stationary for ~ 10 min. The APC inner core barrel is then retrieved, the instrumented shoe is removed, and the data is downloaded into a computer.

A.3.2 Design Features

- The APCT sensor, electronics, and memory are contained in an annular cavity inside the APC coring shoe
- Temperature measurements are obtained without a special wireline trip with a temperature tool
- The APCT toll is deployed on an APC inner core barrel and remains stationary for ~ 10 min in the sediment
- The APCT provides a precise in situ temperature while adding only 10 min to each core barrel run
- The instrumented shoe is removed as soon as the APC inner core barrel is retrieved
- Data are loaded into a computer program for immediate processing
- Hydrocarbon maturity evaluation can proceed during coring to avoid delays for data handling
- The specifications, operating range and limitations of the APC tool are described in Section 4.1 and in the reference of Rack (2001)

A.4 Extended Core Barrel (XCB)

The XCB coring tool is used in sedimentological, climate, and paleoceanographic studies. A schematic of the XCB retractable cutting shoe in standard coring mode is presented in Figure A.4. The XCB shoe extends 6 to 14 in. ahead of the bit in every soft formation and retracts ~ 7 in. (inside the main bit) as weight on bit exceeds about 12000 lb (collapses a coil spring).

A.4.1 Tool Operations

The XCB is used to recover 9.5 m long core samples from soft to moderately hard formations. The XCB is typically deployed when the formation becomes too stiff to piston core (i.e., upon piston coring refusal) or when it is not hard enough to permit efficient recovery with the Rotary Core Barrel (RCB). The XCB cutting shoe extends ahead of the main bit in soft sediments but retracts into the main bit as the weight on bit increases when firm lithologies are encountered. The XCB uses the same Bottom Hole Assembly (BHA) as the Advanced Piston Corer (APC). The XCB relies on rotation of the drill string to advance the hole, and an integral cutting shoe trims the core sample at the same time.

A.4.2 Design Features

- The XCB uses an integral cutting shoe to trim the core
- The shoe is positioned ahead of the main core bit, which reduces core washing (core damage caused by water jets from the shoe nozzles contacting water sensitive formations
- XCB improves core recovery and reduces core disturbance in soft to moderately hard formations
- A unique retraction device allows the XCB, which is normally extended ahead of the core bit, to retract inside the BHA until the cutting shoe is flush with the core bit.
- Cutting shoe is retracted to reduce failures when hard formations are encountered
- An inner core barrel swivel allows the core to remain stationary relative to the formation as the bit rotates, thus reducing the transfer of rotary torque to weakly laminated formations
- XCB reduces discing which is a type of core disturbance caused by transferring rotary torque to the core
- XCB uses the same BHA as the APC Coring System
- The APC and XCB core assemblies can be run in the same assembly, avoiding non-coring time for pipe trips
- In sift formation the cutting shoe option is steel saw-tooth serrated cutting profile hard-faced with tungsten carbide grit
- In hard formations the cutting shoe options are polycrystalline diamond compact, diamond impregnated, surface-set diamond, and thermally stable artificial diamond
- The specifications, operating range and limitations of the APC tool are described in Section 4.1 and in the reference of Rack (2001)

Figure A.6 A Schematic Representation of XCB

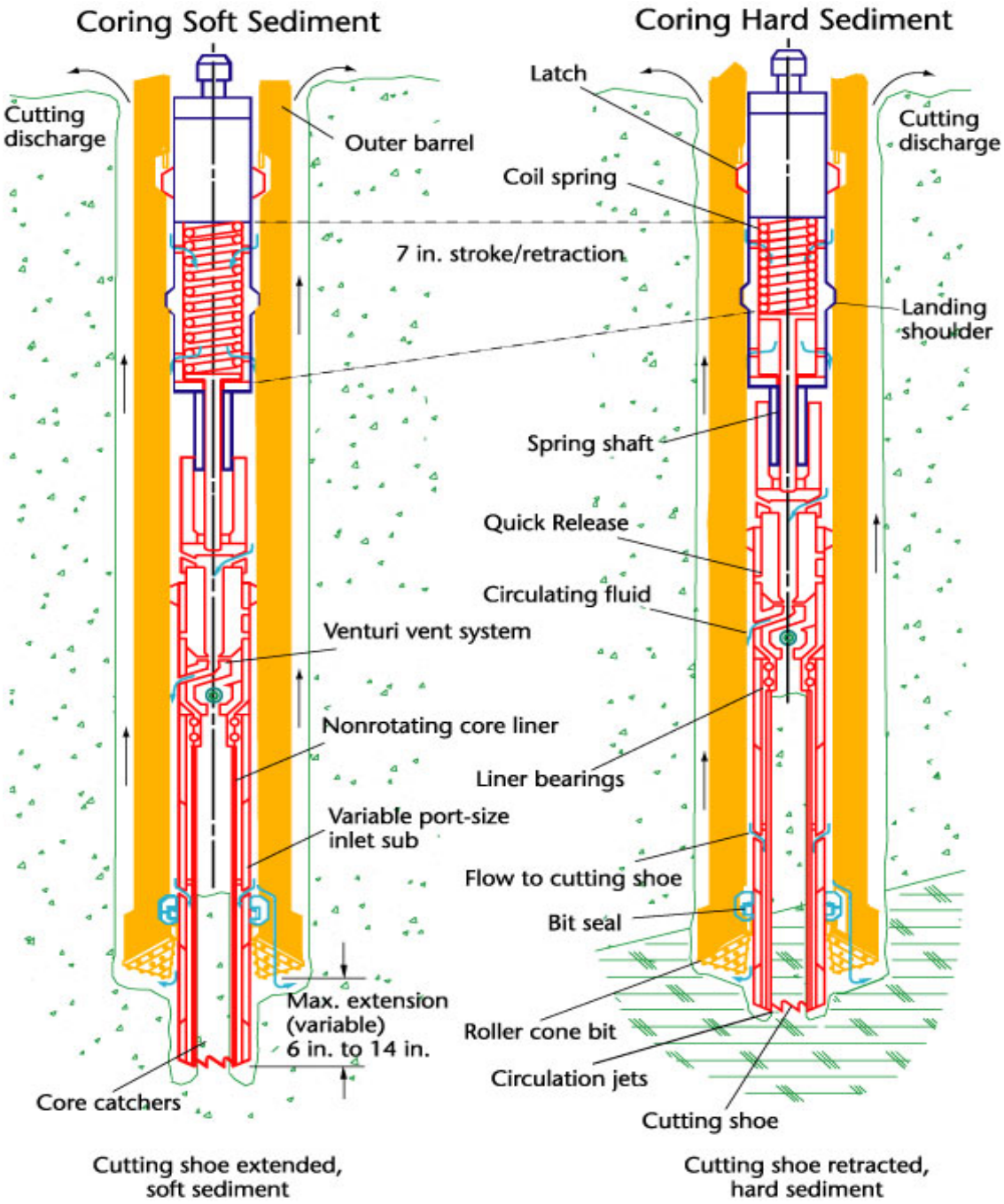
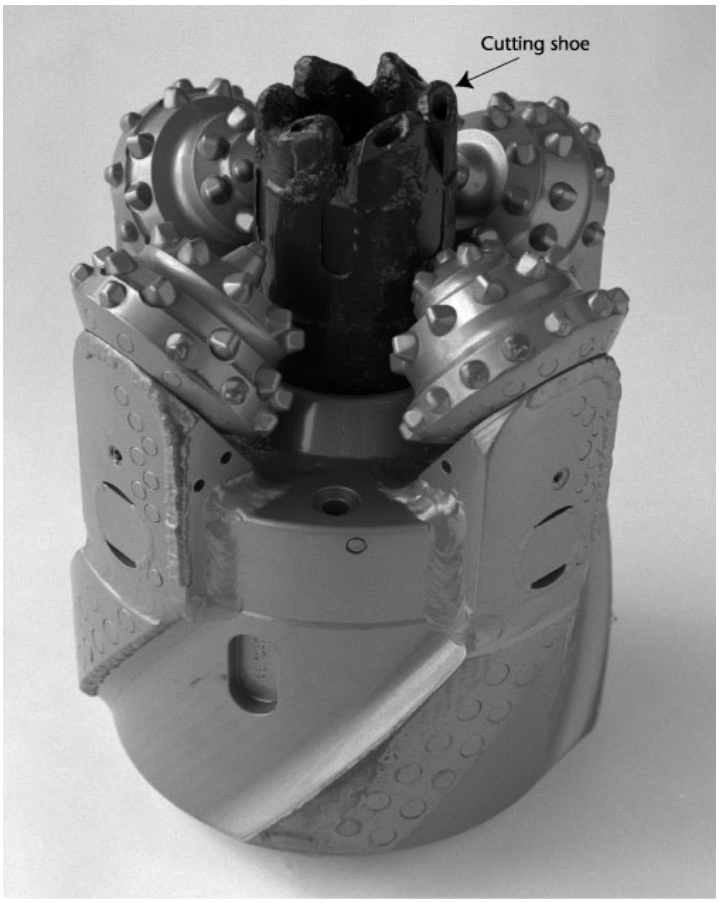


Figure A.7 XCB Coring Bit



A.5 Rotary Core Barrel

The Rotary Core Barrel (RCB) is a rotary coring system designed to recover core samples from firm to hard sediments and igneous basement. The RCB is crucial for oceanic crustal hard rock studies.

A.5.1 Tool Operation

The RCB inner core barrel free falls (and is pumped) through the drill string and latches into the RCB bottom-hole assembly (BHA). The main RCB bit trims the 2.312 in. core. The BHA, including the bit and outer core barrel, is rotated with the drill string while bearings allow the inner core barrel to remain stationary. The inner core barrel can hold a 9.5 m core and is retrieved by wireline. A wireline packoff at the top of the drill string permits rotation and circulation of the drill string to continue while using the wireline to retrieve the core.

A.5.2 Design Features

1) Rugged Design

The RCB BHA, bit, and inner core barrel assembly have a rugged design for use in abrasive and fractured hard sediments and igneous basement.

Benefit: Increases operating time of the bit and improves penetration of hard formations.

2) Drilling with Center Bit

A center bit can be used to drill a hole without attempting to recover core. The center bit is used to drill ahead in hard rock and is run on a special inner barrel sub to lock it into the outer barrel for rotation. The center-bit assembly is configured to allow circulation through the center bit.

Benefit: The center bit can be interchanged with a standard RCB core barrel for "spot" coring.

3) Wireline Logging with Bit Release

A Mechanical Bit Release (MBR) can be operated by wireline to drop a bit in the hole or on the seafloor to provide a fully open BHA for logging.

Benefit: Wireline logs can be run after coring with the RCB system without making a pipe trip to install a logging bit.

RCB Specifications

Inner Core Barrel Length

9.5 m (31.16 ft)

RCB Bit Throat (Core Diameter)

5.87 cm (2.312 in.)

Typical Operating Range

Formation

Firm to very hard sediments and igneous basement

Depth Range

Seafloor through igneous basement

Mean Recovery

20% to 55%

Quantity of Cores on Deck

0.3 to 2 cores/hr depending on water depth and formation hardness

Rate of Penetration

Depends on rock properties, but averages 4.0 to 9.8 m/hr

A.5.4 Limitation

Does not recover soft sediments or granular formations (such as sand, fractured rock, or rubble)

Figure A.8 A Schematic Representation of RCB

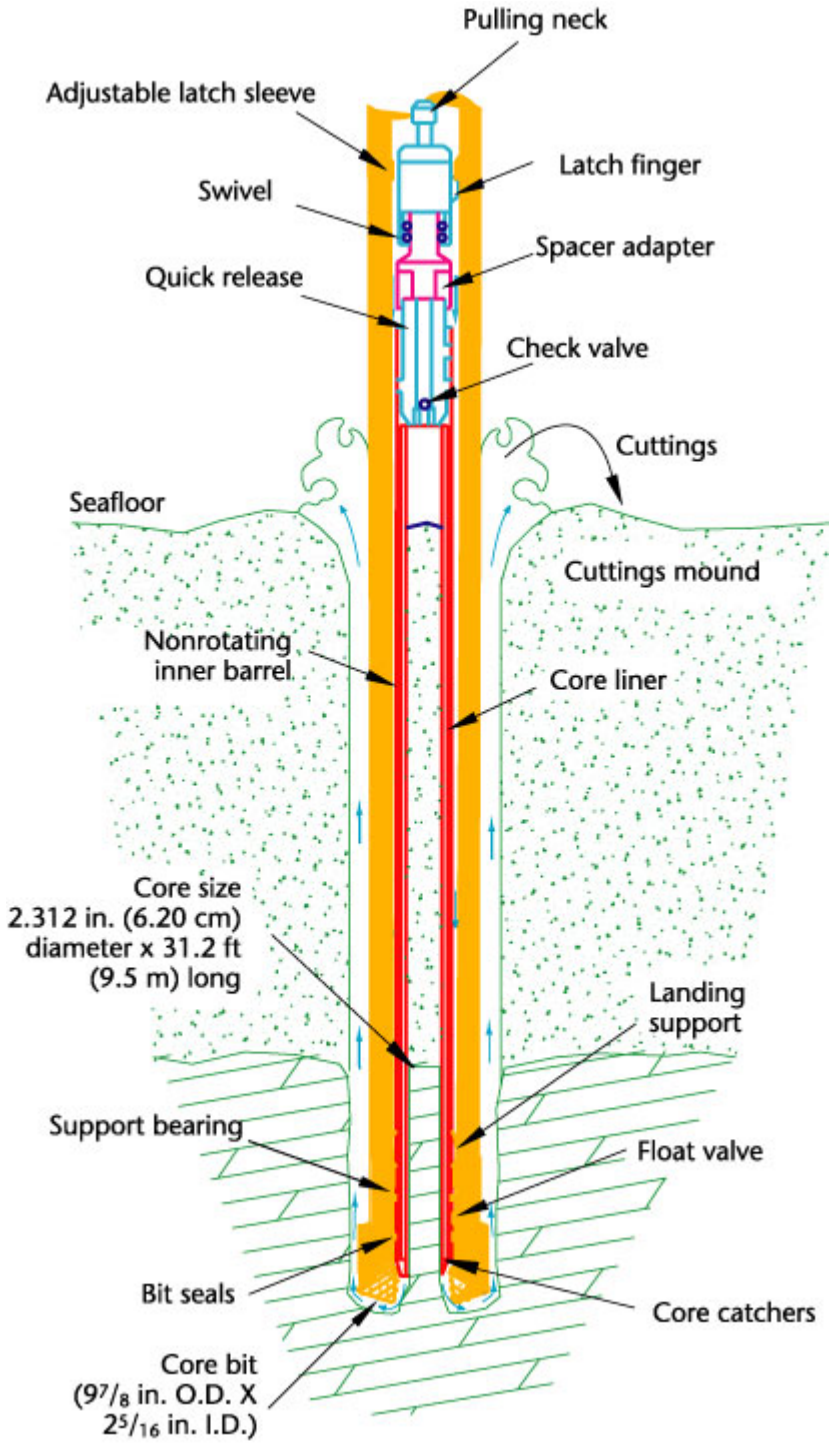
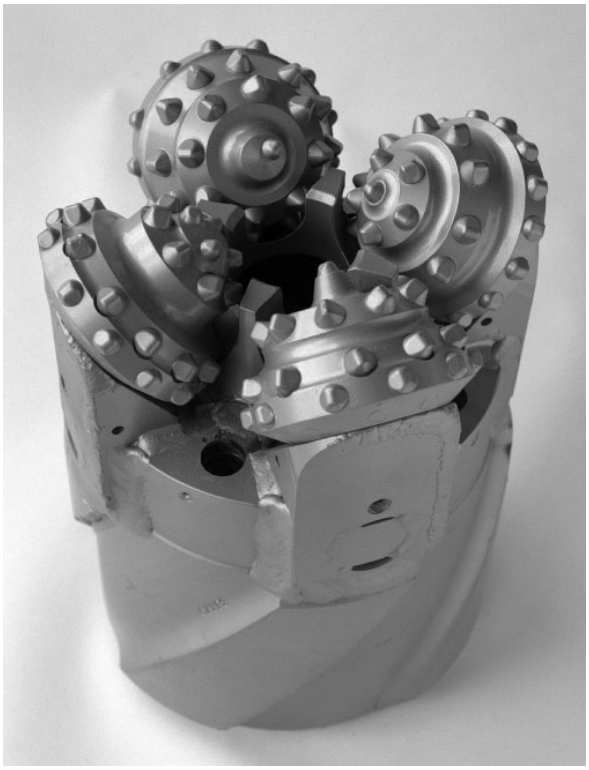


Figure A.9 RCB Coring Bit



A.6 The Davis-Villinger Temperature Probe (DVTP) is designed to take heat-flow measurements in semiconsolidated sediments that are too stiff for the Advanced Piston Corer Temperature (APCT) tool. Coring must be interrupted to take a temperature measurement. The DVTP can also be run on wireline and hung below the bit (when the bit is off bottom) as a temperature logging tool for borehole fluids.

A.6.1 Tool Operation

The DVTP is run through the drill string on a dedicated coring wireline round trip. The DVTP is typically run with the colleted delivery system, which latches into the bottom-hole assembly (BHA). The DVTP probe extends 1.4 m below the bit and is pushed into bottom sediment by the driller with 5000–15,000 lbs and held there for 10 min.

A.6.2 Design Features

1) Compatibility
The tool latches into either the **Advanced Piston Corer**/**Extended Core Barrel** (**APC**/**XCB**) or **Rotary Core Barrel** (**RCB**) BHA.

Benefit: The tool latches into both major coring BHAs, increasing functionality.

2) Probe Length
The robust probe extends 1.4 m below the bit.

Benefit: The probe penetrates into relatively undisturbed sediments ahead of the bit.

3) Decoupled from Heave
The DVTP is deployed on the colleted delivery system, which allows the probe to be disengaged from the BHA after it is pushed into the sediments.

Benefit: This prevents drill string movement (from ship heave) from disturbing the probe while recording formation temperature.

4) Tool Disturbance
An onboard accelerometer monitors tool disturbance while a thermistor records formation temperature.

Benefit: Measures potential tool movement during data recording to assist in interpreting temperature data.

5) Data Collection
The tool is capable of storing eight channels of data for 24 hr when sampling at 3-s intervals. After the tool is recovered, the data is downloaded and calibrated on a computer running ODP LabView software.

Benefit: The DVTP provides sufficient measurement detail and recording time to assure good-quality data.

DVTP Specifications

16-bit analog-to-digital converter

496 Kb of RAM memory

Programmable sample interval from 3 to 10 s

51,000 ohm thermistor temperature sensor

Temperature accuracy ±0.02ºC

Acceleration accuracy ±2 G

Conical probe tip continuously tapered at 2.5º from 55.5 to 8 mm in diameter

Typical Operating Range

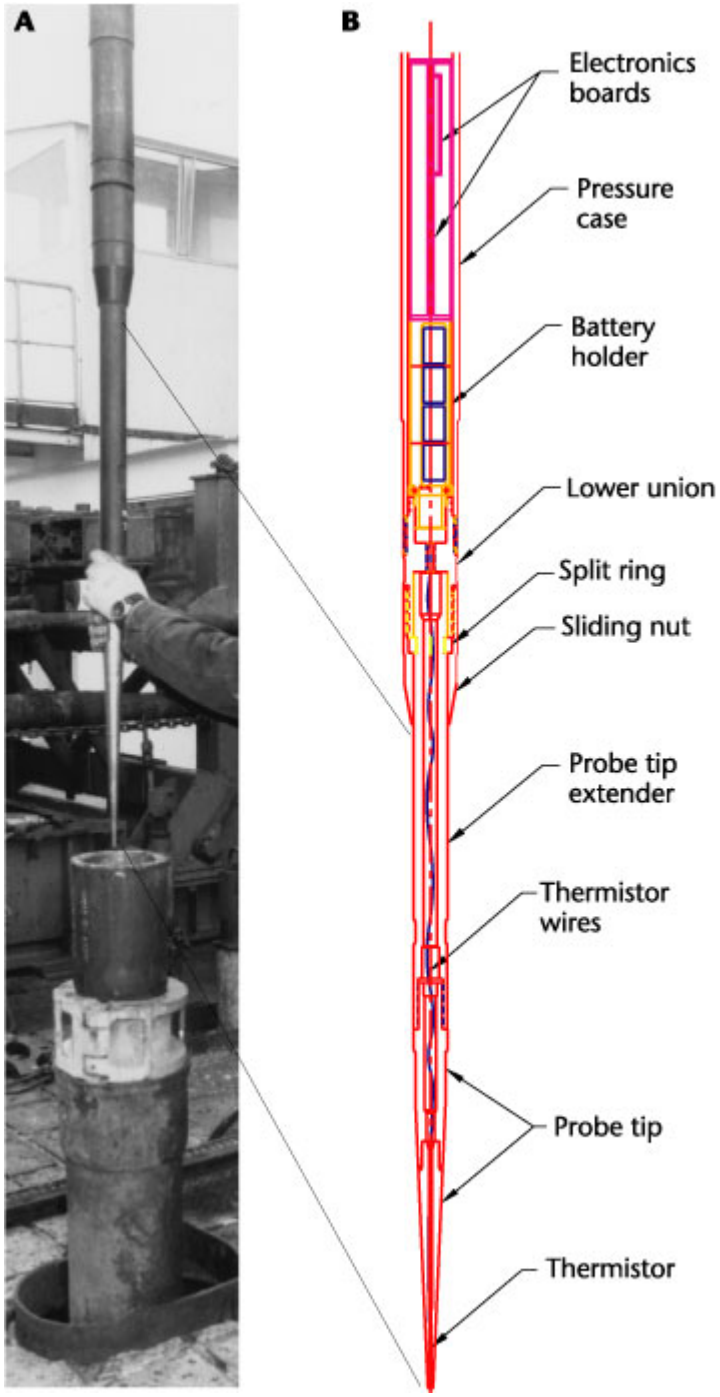
–5ºC to 105ºC temperature measurement range

Soft to semiconsolidated sediments (e.g., chalks or firm clays)

A.6.3 Limitation

Not used in hard rocks (e.g., chert, dolomite, limestone, or basalts)

Figure A.10 A Schematic Representation of DVTP



A.7 Leg 204 ODP (JOIDES) Experience (summer, 2002)

- After two months of Leg 204 ODP expedition in the Pacific Ocean off the Oregon coast, the research vessel JOIDES Resolution docked in Victoria, British Columbia, with a precious payload of methane hydrate samples for scientific study
- The JOIDES Resolution spent from July 6 to September 2, 2002 in the Hydrate Ridge area
- Hydrate samples were collected and preserved in pressure vessels 50 miles offshore
- The area of interest was Hydrate Ridge where two tectonic plates converge and massive accumulations of hydrates are indicated from scientific surveys
- Using the latest in pressure-coring devices, samples were maintained at sub-seafloor pressures after they were brought to the surface so that one might analyze the methane gas trapped inside the frozen ice crystal
- Using specially designed pressure vessels, each six feet long and four inches in diameter, nearly two miles of core were recovered from the ocean floor
- Ice cores in 34 of the vessels are preserved and stored at Texas A&M University for post-cruise investigations
- The presence of hydrates within the sediments in the cores were physically verified
- Many of the cores were used for controlled degassing experiments
- The density contrasts in the cores (a prime indicator of hydrate occurrence) were detected using the newly developed x-ray linear scanner
- The occurrence of hydrates in ocean sediments and in the cores was also evaluated using infrared thermal imaging and a nuclear magnetic resonance logging-while-drilling tool
- Core samples were acquired simultaneously with logging-while-drilling data, allowing a direct comparison of the logging data with the core samples
- Core data and logging-while-drilling data will allow a comparison with a variety of conventional wire line and seismic information to more accurately correlate ocean bottom layers
- Some of the planned scientific investigations were to
  - Investigate variations in the distribution, composition, and concentration of gas hydrates laterally and with depth
  - Sample the sediments, fluids, gases and gas hydrates for correlation, modeling, geochemical, geophysical and historical research, and
  - Figure out what causes variations in the seismic character of bottom simulating reflectors (BSRs), and how BSRs and hydrate occurrence are related
- The database includes paleontological, lithostratigraphic, chemical, physical, sedimentological and geophysical data for ocean sediments and hard rocks.
- Low amounts of H2S were detected at Hydrate Ridge
- A high pressure buildup was seen (3626 psia at 39.2 ^{o}F) as the cores were being brought up to the surface. In some cases, the core liners exploded on deck. Thus, a method of pressure relief is needed to minimize core liner damage and liner failure

Appendix B: HYACE/HYACINTH System (HRC and FPC)

In late 1997, the European Commission began funding a MAST III project called HYACE (short for "Hydrate Autoclave Coring Equipment system"). HYACE was a three year engineering project aimed specifically at developing tools for the recovery and handling of gas hydrates in offshore drilling. By the end of the HYACE project in March 2001, equipment had been developed, some testing of pressure coring tools had taken place on board the ODP drillship JOIDES Resolution in January 2001, but no opportunity to recover gas hydrates had presented itself. To carry the HYACE project forward to the fully operational stage, a new project was proposed to the European Commission project called HYACINTH, which began in December 2001. The HYACINTH project is being carried out by a consortium of six companies and academic institutions from Germany, The Netherlands and the United Kingdom. It was realized from the outset that the success of the HYACINTH project would depend on close collaboration with the international Ocean Drilling Program (ODP). A formal agreement between the HYACINTH partners and the ODP was signed in November 2001. HYACINTH equipment was subsequently deployed on ODP Leg 204.

The equipment tested on ODP Leg 204 included (http://www.geotek.co.uk/hyacinth/):

B.1 Fugro Pressure Corer (FPC) - The percussion corer was developed by Fugro Engineers BV and is known as the Fugro Pressure Corer or FPC. The FPC uses a water hammer driven by the circulation to drive the core barrel into the sediment up to 1 m ahead of the drill bit. The core diameter is 58 mm. On completion of coring, the recovery of the corer with the wireline pulls the core barrel into the autoclave, in which the pressure is sealed by a specially designed flapper valve. The FPC is designed to retain a pressure of up to 250 bar. The percussion corer is suitable for use with unlithified sediments ranging from stiff clays to sandy or gravelly material. In soft sediments it acts like a push corer.

Figure B.1.1 Schematic of Fugro Pressure Corer

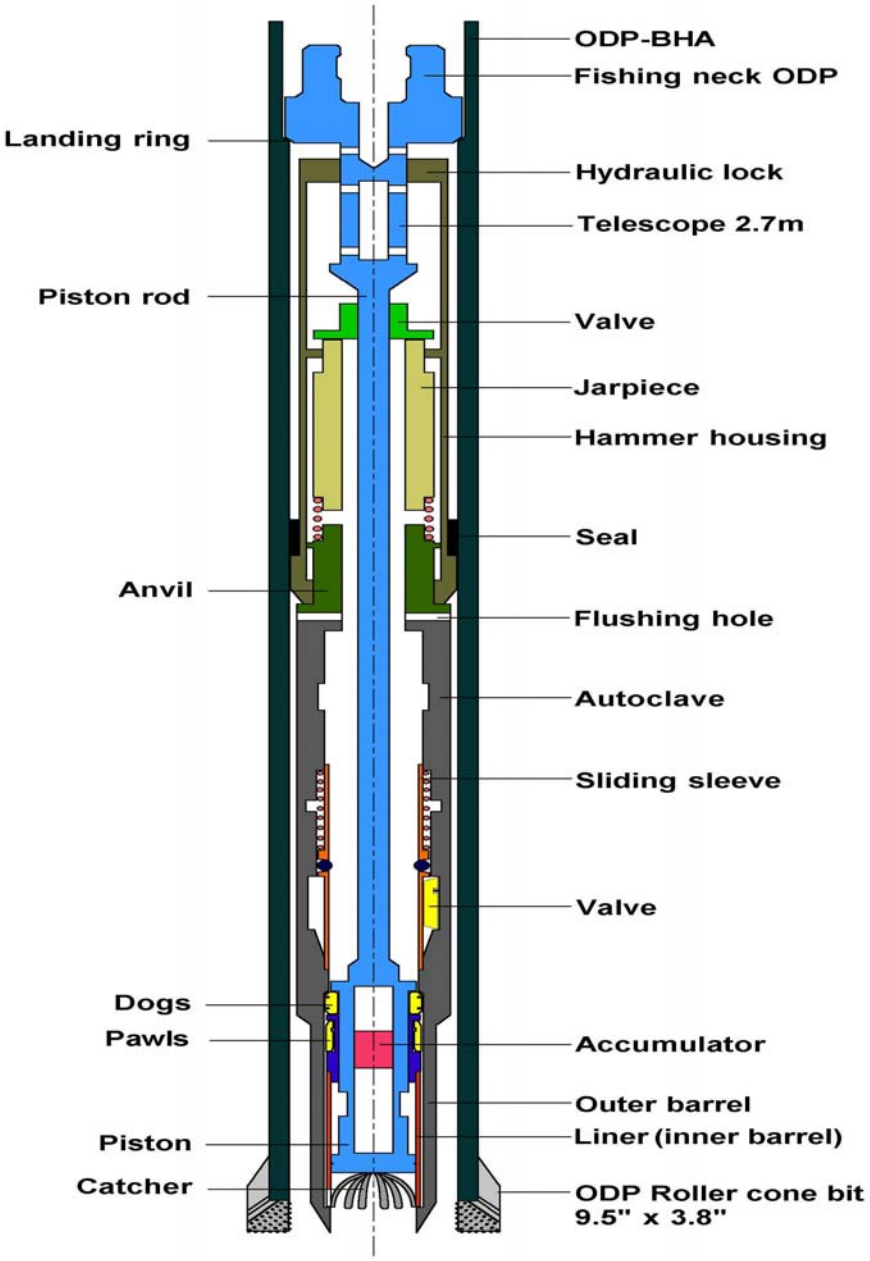


Figure B.1.2 FPC Flapper Valve Assembly

Figure B.1.3 FPC Deployment aboard ODP Joides Resolution

Figure B.1.4 FPC Recovery

Figure B.1.5 Core Transfer

Operational Results:

- 15 minutes for inserting tool into string
- Re-dress time 2 hours
- Good recovery in sand, gravel, stiff clay >500kPa (10 ksf)
- Good drill string stability during tests, no variation of weight on bit
- New valve design had to be fine tuned to close
- Several hydrate cores recovered still under insitu pressure

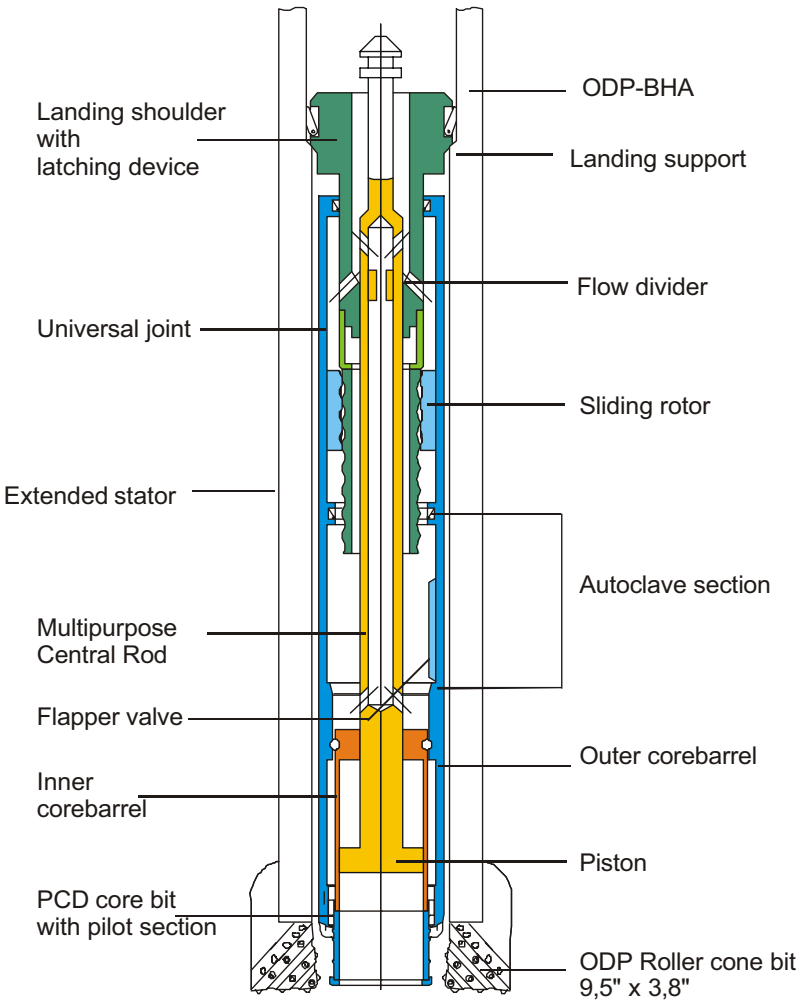
Table B.1.1 FPC Results on ODP Leg 204

Test	Recovery	Valve plate closed	Pressure [bar]	Heave comp P=passive A=active	Remarks
1	100%	-	-	A + P	Top seal
2	50%	Ok	20	A + P	C-line control
3	100%	-	-	A + P	Top seal
4	95%	-	-	A + P	C-line control
5	100%	-	-	A + P	Debris on seat
6	100%	-	-	A + P	Valve blocked
7	100%	-	-	P	Valve blocked
8	20%	-	-	A + P	Liner failure
9	100%	Ok	94	A + P	-
10	100%	Ok	80	A + P	-

B.2 HYACE Rotary Corer (HRC) - The rotary corer was developed by the Technical University of Berlin and the Technical University of Clausthal, and is known as the HYACE Rotary Corer or HRC. The HRC uses an Inverse Moineau Motor driven by the circulation to rotate the cutting shoe up to 1 meter ahead of the roller cone bit. The cutting shoe of the HRC uses a narrow kerf, dry auger design with PCD cutting elements.

This design allows the core to enter into the inner barrel before any flushing fluid can contaminate the material being cored. The core diameter is 50 mm. On completion of coring, the recovery of the corer with the wireline pulls the core barrel into the autoclave, in a similar manner to the FPC, and the pressure is sealed by a specially designed flapper valve. The HRC is designed to retain a pressure of up to 250 bar and is suitable for use in sampling lithified sediment or rock.

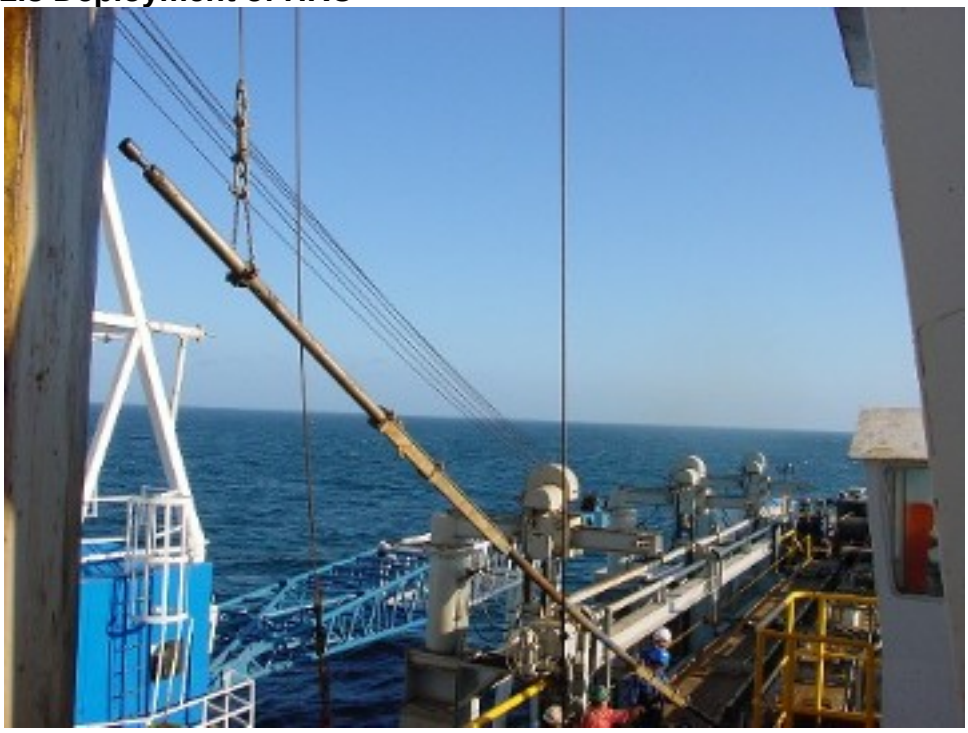
Figure B.2.1 HYACE Rotary Corer (HRC)



HYACE Rotary Corer

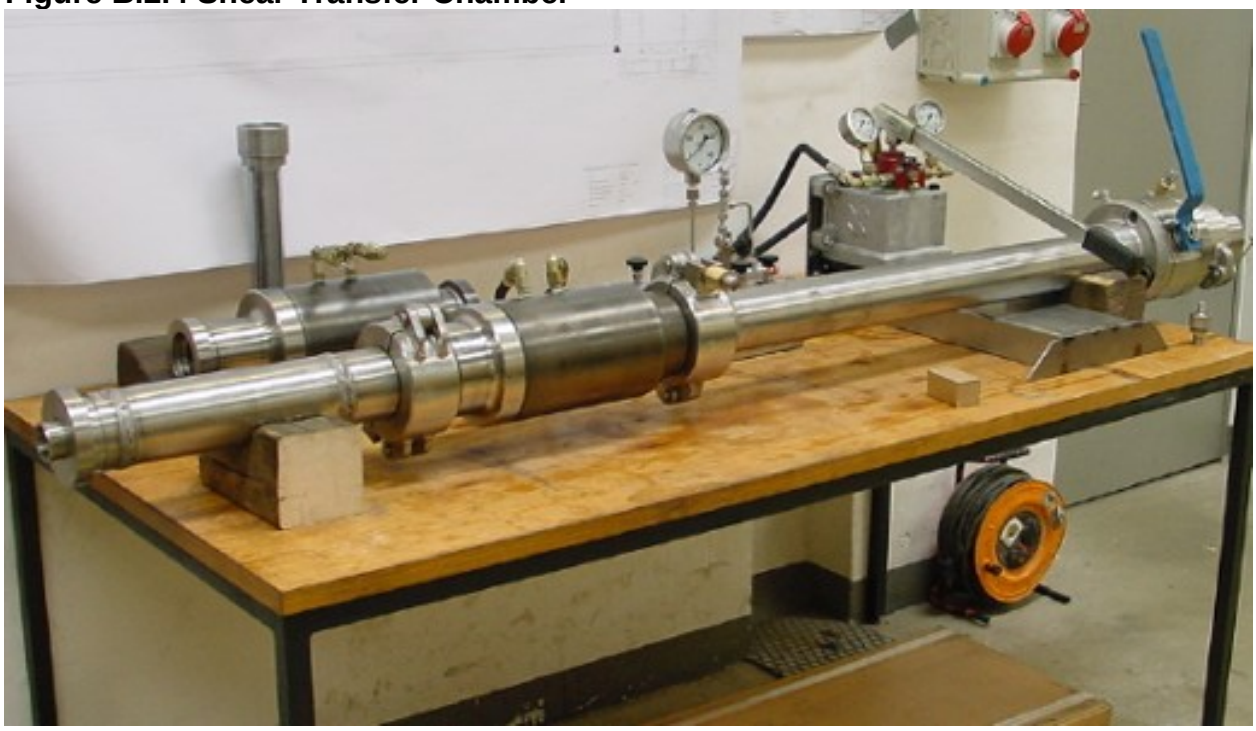
Figure B.2.2 HRC Cutting Shoe

Figure B.2.3 Deployment of HRC



B.2.1 Shear Transfer Chamber (STC) - The pressure core that is preserved in either the FPC or HRC autoclave differs from a conventional atmosphere core in containing many more technical components of the corer. Thus, what is actually transferred under pressure into the first laboratory pressure chamber, referred to as the "Catch Assembly", consists of a "technical part" and a "geological part". Only the geological part needs to be retained under pressure for study. The technical part needs to be extracted from the high pressure environment as soon as feasible in order for it to be re-cycled for further corer deployments. In the case of the FPC, the 1.6 m long Catch Assembly has an upper technical part which is about 0.7 m in length and a geological part about 0.9 m long. A similar Catch Assembly exists for the HRC, with slightly different dimensions.

Figure B.2.4 Shear Transfer Chamber



The purpose of the Shear Transfer Chamber or STC is to separate the technical part of the core from the geological part so that the latter can be transferred under pressure into other chambers for scientific study. The STC can be coupled to the autoclave of either the Fugro Pressure Corer (FPC) or the HYACE Rotary Corer (HRC), to the Logging Chamber or to the Storage Chamber. In order to make the transfer from a corer autoclave, the pressure in the STC is raised to that in the autoclave, the Ball Valve is opened and, with the use of the Manipulator, the pressure core is drawn from the corer autoclave into the STC without loss of pressure. The STC is sealed with its ball valve, the autoclave is de-pressurized and disconnected. A Logging Chamber or a Storage Chamber is then coupled to the STC in the place of the autoclave, raised to the STC pressure and opened to it. Next, the hydraulically operated shearing unit in the STC is used to cut the plastic liner of either the FPC or the HRC core, so that only the

geological part of the core is transferred for core logging and de-gassing. The remaining technical section of the core can subsequently be re-cycled for further deployments of the corer. Note that since the FPC and the HRC cores have different diameters, the STC is supplied with two cutting boxes in order to be able to cope with these different dimensions. The cutting boxes can be quickly interchanged by means of Flange Clamp connections.

Figure B.2.5 Transfer

B.3 Logging Chamber (LC) - Like the STC, the Logging Chamber (LC) is a cylindrical pressure vessel, sealed at one end with a ball valve and at the other by a conical seal fitting to which the Manipulator can be attached for making transfers. The cylindrical part of the LC is manufactured from glass fibre reinforced plastic (GRP), which allows the core contained within it to be geophysically logged with external sensors. An outer steel tube, with longitudinal windows cut into it, allows access for the geophysical sensors and holds the steel end caps in place when the chamber is pressurized.

Figure B.2.6 Logging Chamber

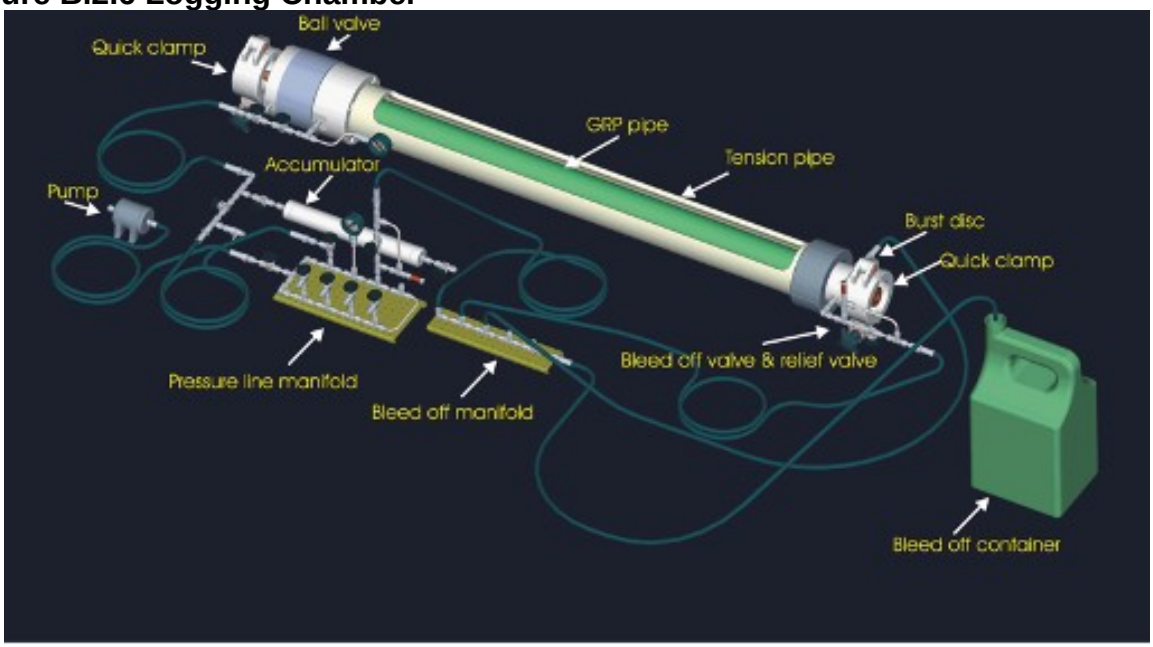
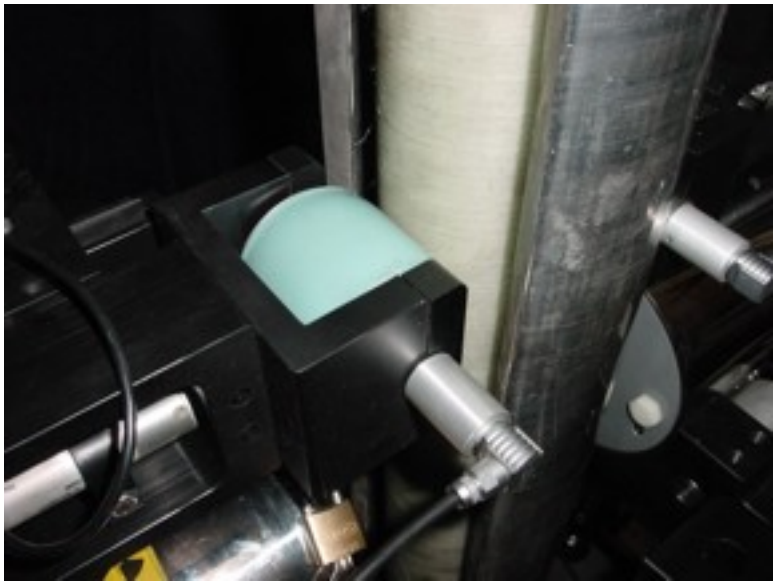


Figure B.2.7 Logging Core

B.2.4 Vertical Multi-Sensor Core Logger (V-MSCL) - The logging of conventional one atmosphere cores is usually done with the core oriented horizontally. For logging cores maintained at seabed pressure inside a Logging Chamber, it is preferable to orient the core vertically. The large quantity of steel in the structure of the LC inhibits the measurement of electrical resistivity and magnetic susceptibility, so the physical properties of the core, which can be logged, are P-wave velocity and Gamma Density. The close up picture shows one of the P-wave rolling acoustic transducers (light blue) pressing against the GRP tube of the LC.

Figure B.2.8 V-MSCL

Figure B.2.9 V-MSCL



B.2.5 Storage Chamber (SC) - The Storage Chamber (SC) is a cylindrical pressure vessel, sealed at one end with a ball valve and at the other by a conical seal fitting to which the Manipulator can be attached for making transfers. The cylindrical part of the SC is manufactured from steel. The SC is designed to preserve a core under pressure for periods of hours to several days, when all available LCs are already loaded with core. Two SCs were used on ODP Leg 204.

B.2.6 Manipulator - The manipulator is a long thin tool used for transferring cores between pressure chambers. It can be coupled to the STC, LC or SC with a Flange Clamp. Since the inside of the Manipulator is exposed to the pressure in the chamber to which it is coupled during a transfer, it is itself a pressure vessel. For the initial transfer, the Manipulator pulls the core out of the corer autoclave into the STC. But for all subsequent transfers, after the core has been cut, it can only push the core from one chamber to another. Click here to see a diagram illustrating the function of the Manipulator with the STC.

All of the pressure corers and laboratory chambers described above have been designed to operate at a maximum working pressure of 250 bar.

B.2.7 Leg 204 accomplishments:

- Hydrate core was recovered from the seabed at in situ pressure, successfully transferred into laboratory chambers without loss of pressure, then geophysically logged.
- For the first time, laboratory measurements have been made of the physical properties of natural hydrates at sub-seafloor pressures without ever releasing this pressure.
- Some cores were then de-pressurised and the gas generated by the dissociation of hydrate was collected and analysed.
- Other cores were preserved and transported to laboratories ashore for more detailed study. The feasibility of preserving and transporting hydrate cores to laboratories elsewhere has been demonstrated.

B.2.7 Operations:

Both the HYACE Rotary Corer (HRC) and the Fugro Pressure Corer (FPC) were prepared and assembled on tool trestles located on the port side of the pipe racker. This area is aft of the derrick, but on the same level as the rig floor. For deployment, a similar procedure was used for both the HRC and the FPC. The tool was first transferred into the vertical position in the derrick, temporarily stored in a rig floor shuck, then deployed in the open drill string.

On retrieval, the pressure corer was returned to its position on the tool trestles for disassembly. The autoclave section of the corer, which contains the core under pressure, was then carried to the platform outside the downhole tools laboratory for examination and connection to the pressure transfer system.

Transferring a pressure core from either the HRC or the FPC autoclave into a laboratory pressure chamber required an open area about 7 m long. First the corer autoclave, Shear Transfer Chamber (STC) and the Manipulator were connected in line, then on completion of the transfer into the STC, the corer autoclave was replaced by either a Logging Chamber (LC) or a Storage Chamber (SC). The platform outside the downhole tools laboratory, on the top floor of the lab stack and just forward of the derrick, proved ideal for this purpose.

When the core transfer had been completed, the LC was taken to the vertical Multi-Sensor Core Logger, installed in a suitable space below decks, for logging.

At various stages during the transfer process and afterwards, the chambers were cooled by the use of ice baths or ice bags in order to maintain the stability of any gas hydrate contained. Chambers were also placed in a refrigerated room for maintaining stable conditions over longer periods of time.

The following table summarises the HYACINTH coring operations on Leg 204. Recovering a core is relatively straightforward and was achieved on most deployments. Recovering a core under pressure is more difficult and requires the corer to function correctly in all respects. In particular, excessive motion of the drill string or coarse sediment stopping the valve from closing properly may prevent the core from being recovered under pressure.

Table B.1 Summary of HYACINTH coring on ODP Leg 204

Wireline Pressure Corer	Number of deployments	Core recovered under pressure	Hydrate core recovered under pressure
FPC	10	2	2
HRC	8	4	3

B.2.8 Future system developments include:

- Development of technologies to allow sub-samples to be taken from pressurized cores without loss of pressure - for chemical, microbiological and petrophysical study.
- Development of equipment for carrying out microbiological experiments on deep sea sediment samples. Our pressure coring system allows barophilic microrganisms to be recovered from the sub-seafloor biosphere and transferred without loss of pressure into laboratory chambers for study.
- Development of a system for electrical resistivity imaging of hydrate cores in pressure chambers. The presence of hydrates in marine sediments has a pronounced effect on their electrical resistivity.