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Hydrate Characterization Research Overview

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HYDRATE CHARACTERIZATION RESEARCH OVERVIEW

by

Rodney D. Malone

Introduction

Gas hydrate research has been focused primarily on the development of a basic understanding of hydrate formation and dissociation in the laboratory, as well as in the field. Laboratory research on gas hydrates characterized the physical system, which focused on creating methane hydrates samples, tetrahydrofuran (THF) hydrate samples, consolidated rock samples, frost base mixtures, water/ice-base mixtures, and water-base mixtures. Laboratory work produced measurements of sonic velocity and electrical resistivity of hydrates. As work progressed, areas, such as the Gulf of Mexico and the Guatemala Trench, where gas hydrates are likely to occur were identified, and specific high potential areas were targeted for detailed investigation. The testing of samples and recovered cores from such areas provided information for detection of hydrate formations in the natural environment.

Natural gas hydrate samples have been tested for thermal properties, dissociation properties, fracture mechanics, and optical properties. Acoustical properties were investigated both in the laboratory and, as possible, in the field. Sonic velocity and electrical resistivity measurements will continue to be obtained. These activities have been undertaken in hydrate deposits on Alaska's North Slope, the Gulf of Mexico and the U.S. East coast Offshore, as well as other gas hydrate target areas.

State of Technology

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

The second factor that controls the distribution of hydrate regimes is the increase of pressure with greater depth, within the defined boundaries. Increased pressure tends to favor the formation of hydrates at greater depths where temperatures are relatively higher. Figure 1 shows the pressure/temperature/depth relationships that are conducive to the formation of gas hydrates. The Hydrate Stability Zone (HSZ) defines the limits for possible formation of natural gas hydrate to the interval from approximately 900 to 4,000 feet at temperatures between +12 and -8 °C. These zones can occur in or adjacent to onshore permafrost areas of Alaska, Canada, and other cold regions. Other major areas of potential hydrate formation exist in the sediments of the world's ocean basins. One theory on offshore HSZ's holds that formation conditions are favorable in areas where the water depth exceeds 1,500 feet; however, actual hydrate formation depths are unknown. Table 1 indicates the estimated thickness

of the HSZ in some of the areas studied (Source is a series of basin studies developed by Geoeplorers International, Volumes 1-15 and funded by DOE/METC).

Table 1. Thickness of the Hydrate Stability Zone (HSZ) in Potential Hydrate Areas

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

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

Natural gas hydrates generally occur beneath the world's seas and oceans where a water column of approximately 1,500 feet exists and where temperatures are appropriate for hydrate stability. These conditions are met in more than 90 percent of the ocean basins. Average thicknesses of the HSZ for the oceans are not well known. The bottoms of probable hydrate deposits have been detected by means of drilling and seismic profiling at depths in excess of 1,000 feet, indicating the possibility of considerable vertical development of the HSZ in the marine environment.

As our understanding of gas hydrate characteristics has advanced through laboratory and field research, so has the diagnostic evaluation of both surface and subsurface geophysical techniques and geochemical analysis of hydrate formations. These characteristics will be valuable in the development of technology to identify features that can aid in locating and defining the gas hydrate reservoir geometry as it exists in the geologic environment. Research is focusing on seismic reflectors, well- logging techniques, and geochemical conditions within the HSZ.

Geophysical Analysis

An understanding of the permafrost regions is an integral part of gas hydrate evaluation, specifically in the onshore environment. During drilling of exploratory and production wells on the North Slope of Alaska, the wellbore is surveyed with a series of well-logging devices that can be used to determine the physical state of the pore waters and permafrost thickness. Logs used in these surveys include resistivity, acoustic transit time, spontaneous potential, gamma ray, caliper, neutron porosity, density, drilling rate and gas chromatograph curves on the mud log. In many wells, the permafrost interval is logged with

only one or two of these devices or not logged at all. The lack of well-log data limits the number of North Slope wells from which the base of ice-bearing permafrost can be determined.

In a study of well logs on Alaska's North Slope, 156 wells selected for the study have at least a resistivity survey through the permafrost zone. The electrical-resistivity and acoustic-transit-time well logs were found to be the most useful in detecting the base of the ice-bearing permafrost. As studies on the North Slope well logs progressed (Collett, T. S., 1983), indications of the use of well logs to detect permafrost and the hydrate stability zone began to be better understood.

One of the early papers dealing with detection of gas hydrates using wireline well logs (Bily and Dick, 1974) studied naturally occurring gas hydrates in the subsurface of the Mackenzie Delta. They discovered that when a gas hydrate was penetrated during drilling, there was a marked increase in the amount of gas in the drilling mud. These gas-hydrate bearing units produced a relatively high resistivity on the dual-induction log and a slight negative spontaneous potential deflection in comparison to an interval containing free gas. In addition, acoustic logs indicated an increase in acoustic velocity for gas-hydrate bearing intervals. The following responses consist of a general review of probable well-log responses within a gas hydrate.

- Mud Log (ML)--On a mud log there is a pronounced gas kick associated with a gas hydrate due to decomposition during drilling. However, if cold drilling fluids are used there may be minimal decomposition of the gas hydrate and little free-gas liberated.
- Dual-Induction Log (DIL)--There is a relatively high electrical-resistivity on this log in a gas-hydrate zone, in comparison to that in a free-gas saturated horizon. The deep-induction resistivity curve is separated from the shallower-reading laterolog-8 resistivity curve, apparently due to gas hydrate decomposition next to the wellbore. If a unit were gas hydrate saturated within the ice-bearing permafrost sequence, the resistivity response on the dual-induction log for the gas hydrate would not be significantly different from that in the surrounding ice-bearing permafrost. Below the base of the ice-bearing permafrost, however, the high resistivity deflection associated with gas hydrate is distinct from the surrounding ice bearing zones.
- Spontaneous Potential (SP)--There is a relatively lower (less negative) spontaneous potential deflection in a gas-hydrate bearing zone when compared to that associated with a free-gas bearing zone. The solid gas hydrate limits the penetration of mud filtrate, thus reducing the negative spontaneous potential. The spontaneous potential curve for the gas hydrate saturated unit within the ice-bearing permafrost sequence would be similar to that in the surrounding ice-bearing units where the mud-filtrate penetration is similarly limited.
- Caliper Log (CL)--The caliper log in a gas-hydrate interval usually indicates an oversized wellbore due to spalling associated with the decomposition of the gas-hydrate. Because the caliper log also indicates an enlarged borehole in ice-bearing permafrost, it is useful only in detecting gas hydrates below the base of the ice-bearing permafrost.

- Acoustic-Transit-Time Log (ATT)--Within a gas hydrate there is a decrease in acoustic transit-time in comparison to a unit saturated with either water or free gas. Because the acoustic transit-time of ice is similar to that of gas hydrate, the acoustic log cannot be used alone to detect gas hydrates within the ice-bearing permafrost sequence.
- Neutron Porosity (NP)--In a gas hydrate there is an increase in the neutron porosity; this response contrasts with the apparent reduction in neutron porosity in a free-gas zone.
- Density Log (Den)--Within a gas hydrate there is a decreased density in comparison to a unit saturated with water. Because the density of ice is similar to that of gas hydrate, the density log cannot be used independently to identify a gas hydrate within the ice-bearing permafrost.
- Drilling Rate (DR)--In a gas hydrate the relative drilling rate decreases, due to the solid nature of the gas hydrate. There is a similar drilling rate response within ice-bearing permafrost, and, therefore, drilling rate change is not useful as a fast hydrate detector within the ice-bearing permafrost sequence.

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

There have been strong indications of hydrate accumulations in the offshore environment during drilling and coring of certain formations. The widespread occurrence of a bottom simulating reflector (BSR) has been noted in the marine environment from seismic records obtained in widely separated areas of the world's oceans (i.e., Black Sea, Gulf of Mexico, Bering Sea, Beaufort Sea, U.S. Atlantic Coast, and U.S. Pacific Coast). The BSR is believed to be an anomaly that is caused by a consolidated (frozen) zone in the bottom sediments, overlying an unconsolidated zone of sediments containing free gas. Analysis of the HSZ in the regions of the BSR indicates that the geothermal gradient intersects the stability curve at or near the lower boundary of the BSR. Since the sonic velocity of the hydrate-filled sediments is lower than that of unfrozen or conventional gas reservoirs, the BSR appears to indicate the base of the gas HSZ. Table 2 shows the BSR depths and areal extent of study areas in U.S. waters.

Open-hole geophysical logs also strongly suggested the presence of naturally occurring, in situ gas hydrates. The mud log indicated that a significant amount of free gas was liberated from the hydrate interval during drilling. Logs, such as the dual induction and the compensated sonic, indicated the presence of hydrates with anomalously high resistivities and transit times within the suspected gas hydrate zone. A recovered hydrate sample had a gas composition of 92.79 percent methane, 7.19 percent nitrogen, and minor traces of carbon dioxide, ethane, and propane.

Table 2: Bottom Simulating Reflectors (BSR's) in Potential Gas Hydrate Areas

Area	BSR Depths (feet)	Water Depths (feet)	BSR Areal Extent (square miles)
Beaufort Sea	300-900	1,200-7,400	6,562-20,072
Bering Sea	1,640	1,500-9,000	nd*
Aleutian Trench	3,000	13,500	nd
Gulf of Alaska	1,710-2,008	4,800-3,566	nd
Offshore Northern California	541-929	2,400-3,560	2,000
Blake Outer Ridge	1,476-1,870	8,200-11,480	12,352
Baltimore Canyon	820	6,562-15,093	20,458
Gulf of Mexico	100-2,620	1,312-13,124	3,088

* Not determined.

The occurrence of hydrates identified in well-log analyses indicates that the controlling characteristics for hydrate formation are localized, forming disseminated deposits with varying hydrate concentrations. While massive blanket deposits of gas hydrates do occur, they do not generally occur in large quantities within the sediments of the hydrate stability zone. The massive deposits will generally occur near the base of the hydrate zone or where large quantities of gas from some source are released within the HSZ. Well-log analysis methods, however, cannot detect the most common form of hydrates (disseminated) in low-porosity sediments. Evaluation using Well-Log methods is limited to detectable concentrations and requires the use of more than one type of well-log. Porosities and permeabilities of the matrix material also must be high enough to allow the flow of water and gas because sufficient quantities are necessary to form hydrates.

A new suite of logs, which permits the distinction between conventional reservoirs and the hydrate reservoir, is needed. The carbon/oxygen log shows promise as an analytical tool, as it can differentiate between water and hydrates. The detection of gas hydrates is possible using the sonic and electrical resistivity logs now in existence. Other tools that may be useful are the density log, carbon/oxygen log, and nuclear magnetic resonance (NMR) log. Some of these logs are relatively new and interpretative techniques need to be developed or modified. Geophysical methods such as seismic surveying are also effective in hydrate detection (i.e., the bottom simulating reflector (BSR)).

Future Trends

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

Seismic surveys within the Blake Outer Ridge area have resulted in the identification of BSR'S, interpreted to be a reflection from the gas/gas-hydrate contact at the base of the HSZ. Assuming that the BSR is the base of the HSZ, the areal extent of the hydrate zone can be mapped. The areal extent identified

by BSR's is approximately 20,000 square miles. The subbottom depth to the BSR for the area is approximately 1,880 feet. If one were to calculate the available pore volume for hydrate formation, assuming 30 percent porosity, the maximum pore volume would be $20,000 \text{ mi}^2 \times 1,880 \text{ feet} \times .30 = 940 \text{ tcf}$. Geophysical and other technologies, such as geochemical diagnostics, can provide reasonable interpretations and models of a gas hydrate reservoir.

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Gas Hydrate Stability Zone

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Figure 1.

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