

PRESSURE CORE ANALYSIS: THE KEYSTONE OF A GAS HYDRATE INVESTIGATION

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ABSTRACT

Gas hydrate investigations are converging on a suite of common techniques for hydrate observation and quantification. Samples retrieved and analyzed at full in situ pressures are the "gold standard" with which the physical and chemical analysis of conventional cores, as well as the interpretation of geophysical data, are calibrated and groundtruthed. Methane mass balance calculations from depressurization of pressure cores provide the benchmark for gas hydrate concentration assessment. Nondestructive measurements of pressure cores have removed errors in the estimation of pore volume, making this methane mass balance technique accurate and robust. Data from methane mass balance used to confirm chlorinity baselines makes porewater freshening analysis more accurate. High-resolution nondestructive analysis of gas-hydrate-bearing cores at in situ pressures and temperatures also provides detailed information on the in situ nature and morphology of gas hydrate in sediments, allowing better interpretation of conventional core thermal images as well as downhole electrical resistivity logs. The detailed profiles of density and V_p , together with spot measurements of V_s , electrical resistivity, and hardness, provide background data essential for modeling the behavior of the formation on a larger scale. X-ray images show the detailed hydrate morphology, which provides clues to the mechanism of deposit formation and data for modeling the kinetics of deposit dissociation. Gas-hydrate-bearing pressure cores subjected to X-ray tomographic reconstruction provide evidence that gas hydrate morphology in many natural sedimentary environments is particularly complex and impossible to replicate in the laboratory. Even when only a small percentage of the sediment column is sampled with pressure cores, these detailed measurements greatly enhance the understanding and interpretation of the more continuous data sets collected by conventional coring and downhole logging. Pressure core analysis has become the keystone that links these data sets together and is an essential component of modern gas hydrate investigations.

Keywords: gas hydrate, pressure core, core analysis, borehole logging, porewater geochemistry, thermal imaging, electrical resistivity, Archie's relationship

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INTRODUCTION

The need to assess the nature, distribution and concentration of gas hydrate in the marine environment is driven by multiple interests. Marine gas hydrate is important to the oil industry, not just as a potential energy resource, but also as a significant oilfield geohazard. Scientific interest in gas hydrate often focuses on the overall carbon cycle and the role hydrates might play in climate change. However, in the last few years, the biggest financial input into marine gas-hydrate-related drilling expeditions has come from national governments and their associated national energy and geological organizations. The hope here is to use gas hydrate resources within their territorial borders to help achieve a higher degree of energy independence.

Since 2002 there have been a number of dedicated expeditions around the world where the primary goal has been to determine the nature, distribution and concentration of marine gas hydrate throughout the gas hydrate stability zone at a number of sites. These include Ocean Drilling Program (ODP) Leg 204 to Hydrate Ridge, Oregon Margin [1]; the Chevron/DOE (US Department of Energy) Naturally-Occurring Hydrates JIP (Joint Industry Project), Gulf of Mexico [2]; Integrated Ocean Drilling Program (IODP) Expedition 311, Cascadia Margin [3]; the Indian National Gas Hydrate Program Expedition 1 [4], Bay of Bengal; the Chinese Guangzhou Marine Geological Survey Expedition 1 [5], South China Sea; and the Korean Ulleung Basin Gas Hydrate Expedition 1, East Sea [6].

All these expeditions employed a variety of techniques based around the drilling of boreholes (located mainly on the basis of seismic analysis) to investigate the gas hydrate regime in relation to the tectonic and sedimentary setting. One common feature of all these expeditions is that they all used the various analyses of pressure cores as reference points with which to compare and calibrate observations from the other techniques. Pressure core analysis has now become a routine part of gas hydrate investigations and here we summarize how the data acquired from pressure cores relates to other data typically obtained and how it can form the keystone of well-planned gas hydrate drilling expeditions.

PRESSURE CORE ANALYSIS

Gas-hydrate-bearing sediments sampled by conventional (non-pressure-retaining) coring

techniques are often highly disturbed by gas hydrate dissociation and gas exsolution during recovery. Pressure coring alleviates these effects enabling samples to be recovered that are relatively undisturbed and suitable for detailed examination.

The analysis of pressure cores provides unique data sets in gas hydrate environments that cannot be obtained by other techniques. First, the concentration of methane and other light hydrocarbon gases, and by inference the amount of gas hydrate, can only be obtained from pressure core analysis. Fine-scale morphological examination of gas hydrates in sediments can be achieved with these “undisturbed” samples, brought to the surface without any hydrate dissociation. Finally, physical properties of hydrate-bearing-sediments are best measured either in situ or from high-quality pressure cores. All these parameters are crucial to our understanding of formation, evolution and the potential exploitation of the marine gas hydrate environment. Pressure core analysis therefore plays an important role in gas hydrate investigations, and can provide unique ground-truth data for other gas hydrate techniques.

Only a few borehole pressure coring tools have been developed and used in gas hydrate environments and only the HYACINTH system currently lends itself to detailed pressure core analysis [7]. Detailed core analysis is achieved with this system because the Pressure Core Analysis and Transfer System (PCATS) enables the cores to be maintained and handled at in situ pressure [8]. Pressure core handling involves all the processes of removing the core from the coring tool, manipulating the core through nondestructive measurement apparatus, and transferring the core into other storage or measurement chambers.

A typical history of a pressure core following recovery at the drill floor begins with nondestructive testing or “core logging” followed by careful depressurization enabling the concentration of gas hydrate to be accurately determined. Alternatively, after the nondestructive testing, the cores can be stored at in situ pressures for further analysis at a later date on shore, or they can be depressurized rapidly for storage in liquid nitrogen and further analysis at atmospheric pressure. The latter technique is prone to significant sample disturbance, but fine scale

structures of gas hydrate morphology can be largely preserved [9].

Pressure Core Logging

Nondestructive testing of HYACINTH pressure cores takes place immediately the core is transferred from the coring autoclave using the PCATS. The nondestructive core analysis component of the PCATS is the MSCL-P (Multi-Sensor Core Logger-Pressure), which is used routinely to collect non-destructive data on HYACINTH pressure cores, including gamma density, P-wave velocity, and X-ray images.

Gamma density is measured using a gamma ray attenuation technique across the aluminum pressure chamber and core. Changes in density primarily reflect changes in lithology if the gas hydrate concentrations are low. This is especially true when the gas hydrate occurs in a “pore filling” form, as there is only a small difference in density between the normal pore-filling fluid (nominally 1.02 g/cc) and methane gas hydrate (nominally 0.92 g/cc). However, when massive or “grain displacing” gas hydrate occurs in veins or nodules, changes in the average density (caused by the hydrate replacing the denser sediment framework) becomes more obvious as low density features or zones. The density of the sediments is an important parameter that not only helps distinguish gas hydrate and different sediment facies but it is also used quantitatively to estimate porosity. This in turn is used to calculate the total pore volume in the core enabling the concentration of gas hydrate to be determined accurately from the depressurization experiments (see below).

The ultrasonic P-wave velocity (V_p) is determined from the travel time of ultrasonic pulses between two transducers mounted on either side of the core inside the pressure chamber. Velocities are often little changed at low gas hydrate concentrations, but significant pore-filling hydrate will cause increases in velocity if grain cementation occurs. In solid hydrate, velocities can be higher than 3000 m/s, compared with normal unconsolidated sediments with velocities typically in the 1500-1800 m/s range. With varying morphologies of “grain displacing” gas hydrate, average velocities can increase significantly, although when the hydrate is in the form of thin veins velocities can be difficult to measure due to waveform interference effects from the complex structures. Velocity anomalies are thought to be a key parameter for the interpretation of the occurrence of gas hydrate from seismic records.

Information from both these small-scale core measurements and the larger-scale companion borehole sonic measurements will increase our understanding of how seismic velocities are related to natural gas hydrate concentrations and morphologies in sediments.

X-ray images are obtained through an aluminum pressure chamber using a linear X-ray imaging system consisting of a lead-shielded microfocal X-ray source and phosphor image intensifier. The intrinsic spatial resolution of the images is approximately 150 μm . Some typical examples of the complete non-destructive data set collected from HYACINTH pressure cores containing gas hydrate have been presented previously [1, 3, 4, 8]. Many examples have now illustrated that it is common to observe grain-displacing gas hydrate structures in clay-rich sediments. X-ray images of pressure cores have revealed gas hydrate nodules, horizontal lenses, and subvertical veins. Further confirmation of the complex nature of the vein structures present can be obtained either by rotating the core while in the X-ray beam or by performing full post cruise X-ray computed tomographic (CT) analysis [10].

This morphological structure of gas hydrates within the sediment column is important for many reasons. Gas hydrate formation and growth is poorly understood and detailed observations of the in situ morphology are likely to help explain these mechanisms. Conversely the detailed morphology of gas hydrates will affect the rates and nature of gas dissociation under the influence of increasing temperature or decreasing pressure. Models predicting the behavior of gas-hydrate-bearing sediments during dissociation, whether for well-bore stability, geohazard assessment, or potential methane gas production, must acknowledge the sometimes very complex nature of gas hydrate morphologies in fine-grained sediments.

Depressurization/Hydrate Concentration

One of the primary reasons for collecting pressure cores is to accurately determine the concentration of gas hydrate present. Mass balance analysis from the careful depressurization of pressure cores is the only way to accurately quantify the total concentration of natural gas in a core. From these measurements the gas hydrate saturation of a sediment can then be calculated assuming dissolved gas, free gas, and gas hydrate phases are in thermodynamic equilibrium. The slow isothermal release of pressure from a pressure core allows gases to exsolve from pore fluids and gas

hydrate to dissociate. Measuring the quantity of gas, its composition, and its evolution relative to time and pressure in a depressurization experiment provides information on the quantity, composition, and surface area of gas hydrate [11, 12, 13]. The original experimental procedures for these degassing experiments have been refined more recently to take account of the water expulsion that occurs when the cores are depressurized [3, 4]. In practice most experiments are not performed isothermally as it can take a long time to fully depressurize a core (perhaps 1-2 days). A realistic period may be 1-4 hours depending on the amount of gas hydrate present. The total amount of gas contained in a pressure core is then compared to the pore volume of the core, and gases that were present at a level beyond saturation at in situ conditions are assumed to exist as a gas hydrate or free gas phase.

Any pressure core can be used for this total gas collection, but to calculate the concentration of gas hydrate present an assessment of core volume and pore volume is required. These measurements can currently be achieved at full pressure in the MSCL-P with the HYACINTH pressure cores. Accurate assessments of total sediment volume and density are obtained from a combination of the X-ray images and the gamma density measurements. This provides values of core volume and porosity and hence total pore volume. When depressurizing cores inside the MSCL-P, it is also possible to observe the onset and evolution of gas as the dissociation process progresses. This provides added insights into the distribution of gas hydrate within the core even when the hydrate is not clearly visible on the original X-ray images.

Data that shows the sediment is under-saturated in methane is also extremely important, as pressure core depressurization is the only technique that can positively confirm the absence of gas hydrate. Plotting methane concentration, both above and below saturation, relative to the changing thermodynamic boundaries downhole allows visualization of the methane gradient and is a requirement for definition of the potential zone of gas hydrate occurrence .

Not only do X-ray images obtained during depressurization clearly indicate where the gas hydrate is dissociating from, measurements of the changing physical properties of the sediment-hydrate matrix during dissociation will be critical for any study of gas hydrate production as a resource or gas hydrate geohazard assessment.

Measurements of physical properties during these depressurization/production tests have also been made onshore in a companion measurement chamber developed at Georgia Tech., the Instrumented Pressure Testing Chamber (IPTC) [14]. This instrument has the advantage of being able to drill holes in plastic core liner and insert probes into the sediment enabling measurements such as electrical resistivity, shear wave velocity and strength to be made.

Additional testing of pressure core samples

The PCATS enables cores to be transferred at in situ P/T conditions in and out of different chambers for a number of applications. One of the most important of these is the ability to store the core in a storage chamber that enables further laboratory experiments to be performed at a later date. Storage chambers have been fabricated with aluminum alloy enabling further detailed X-ray CT analysis to be performed [4, 6, 8, 10]. Cores kept in storage chambers and transferred to land-based laboratories also enable other experiments to be performed when time is not at a premium as it often is offshore. These measurements can include slow isothermal depressurization/production tests as well as the IPTC measurements mentioned above.

For other specialized experiments (e.g. microbiological or geochemical) there is a need to subsample the pressure core and isolate particular sections while retaining the in situ pressure. Special apparatus has been built and used for these purposes enabling microbial growth experiments to be conducted [7]. With further development the PCATS will be able to cut subsamples under pressure and transfer them into custom-built chambers for detailed testing of other parameters. For example, there is currently no way to artificially create or simulate the complex morphologies of natural gas hydrates in laboratory samples for geomechanical testing. With the requirement to obtain better data for geohazard and production modeling, there is a pressing need to get undisturbed pressure core samples of sediments containing natural gas hydrate into sophisticated geotechnical test chambers, which will soon be realized.

INTEGRATING HYDRATE TECHNIQUES

The gas-hydrate-related data collected on pressure cores is not only important in its own right; it is also key ground-truth data for other, more indirect measures of gas hydrate that are used to quantify gas hydrate and determine the gas hydrate

distribution. Pressure cores typically comprise less than 10% of a cored section in a borehole; 30–90% of the remaining sediment is generally recovered by conventional non-pressure coring. Non-pressure coring in gas-hydrate-rich sediment sequences can be dogged by pore recovery caused by the destructive effects of methane gas expanding, both from gas hydrate dissociation and gas exsolution. It is inevitable that the worst recovery rates always coincide with the most gas hydrate and this observation in its own right is valuable. However, at lower overall gas hydrate concentrations significant core recovery can be achieved and useful measurements made from thermal imaging and pore water chemistry that relate to the occurrence and concentration of hydrates. The properties of any sediment not recovered in cores must be inferred from downhole geophysical measurements. By applying the pressure core data to the data sets collected by conventional coring or downhole measurements, a more quantitative gas hydrate distribution throughout the entire gas hydrate stability zone can be established.

Thermal Imaging

Natural gas hydrate dissociates when recovered in non-pressure cores. The endothermic nature of this process creates cold anomalies in the core itself as heat is absorbed from the surrounding sediments and the core liner. Identification and quantification of these cold spots provides a quick means of locating dissociated, or dissociating, gas hydrate within cores [15]. Infrared thermal imaging of these cold spots along the length of all recovered cores creates a semiquantitative hydrate data set, which, when combined with pressure core and porewater groundtruth data, can become a continuous quantitative record of gas hydrate abundance downhole.

The cold anomalies created on the surface of the plastic core liner are best detected with an automated infrared camera that scans the core as soon as possible after recovery [3, 4] although probe measurements made in the center of the core provide a better estimate of the true degree of cooling which has occurred. The thermal imaging of cores is primarily used as a qualitative tool for quickly determining the distribution of gas hydrate present in the core, enabling samples for geochemistry (see below) or other studies to be obtained rapidly.

In sediment sequences where the gas hydrate is in relatively low concentrations and/or in thin layers,

then the near complete core recovery and continuous thermal imaging data sets lend themselves to a quantitative interpretation. This quantitative use of infrared thermal images is hampered by the many variables that can influence the rate of gas hydrate dissociation and diffusion of the resultant thermal anomalies, including the rate of core recovery, the mechanical/thermal properties of the corer, the temperature profile in the water column, gas hydrate morphology/surface area, thermal properties of the surrounding sediments, and the air temperature on deck. Gas expansion and gas exsolution can also induce cooling. However, the energy removed from the cooled regions of the core can be used in a semi-quantitative manner, as a minimum estimate of gas hydrate dissociated in the core [15]. If these semi-quantitative estimates are compared to the quantitative estimates from pressure cores and porewater freshening analysis (below), the data may be empirically adjusted to better represent the total distribution of gas hydrate in the cored interval.

Porewater Geochemistry

When cores containing gas hydrate are depressurized, the resulting dissociation of gas hydrate releases methane and freshwater. One cc of methane hydrate releases approximately 164 cc of methane at standard temperature and pressure—and 0.8 cc of fresh water. Most of the methane gas escapes from the core, but the fresh water remains, diluting the pore fluids. This pore water freshening effect is commonly used not only as an indication of the in situ presence of gas hydrate but as a quantitative measure of the amount of hydrate present in the sediments. Chlorinity of the porewater is measured to monitor this freshening, as chloride ion is conservative in the porewater [16, 17, 18, 19]. Quantitative measurement of gas hydrate using porewater freshening analysis requires knowledge of the in situ porewater geochemistry for comparison, and depressurized pressure cores can provide this data.

As chlorinity analysis is a discrete measurement, made on only a portion of the core, sample selection is critical. Sample selection guided by infrared imaging allows samples to be taken both inside and outside thermal anomalies (putative gas hydrate). It is important to ensure that sufficient measurements are taken in areas where no thermal anomalies are detected in an attempt to establish a reliable baseline (see below). It is also essential to determine the extent of contamination by drilling fluids; typically porewater sulfate is measured and

used as a tracer of surface seawater. Assuming sulfate is already depleted in the sedimentary sequence of interest, the sulfate values can be used to discard or correct chlorinity variations due to infiltration of drilling fluids caused by sample disturbance.

The accuracy of the quantitative assessments of gas hydrate from porewater freshening is largely dominated by the accuracy and confidence in the background chlorinity values, i.e., the in situ values of chlorinity (prior to any gas hydrate dissociation). At a number of gas-hydrate-bearing sites, strong gradients and variations in measured chlorinity have been observed that are thought not to be an effect of gas hydrate dissociation [3]. Consequently, it is not realistic to assume constant chlorinity values with depth and it is normal to assume that only chlorinity excursions from a baseline curve are caused by hydrate dissociation. However, invoking this assumption precludes the ability to determine the occurrence of gas hydrate that varies smoothly in concentration through the section. To resolve this “baseline problem” an independent assessment of the in situ values of pore water chlorinity is required.

Ideally, in situ chlorinity values would be obtained by in situ sampling, but this is not yet a routine procedure. In situ values have sometimes been calculated from downhole resistivity logs [20]. However, as has been pointed out elsewhere [21] the results are strongly dependent on the estimated Archie’s relation parameters and are subject to the same uncertainties as direct hydrate estimations from resistivity logs (see below).

Values of chlorinity taken from depressurised pressure cores resolve this dilemma by providing confirmation (or otherwise) of assumed baseline values. The gas hydrate quantity from methane concentration can be reconciled with chlorinity data from the same core, and the baseline chlorinity calculated for each pressure core. These points from pressure coring anchor the chlorinity baseline. In this way an accurate in situ chlorinity profile can be established from relatively few pressure cores, enabling the more numerous porewater freshening data points from the non-pressure cores to be used as accurate assessments of gas hydrate concentration.

Borehole Logging

Borehole geophysical logging (Logging While Drilling, LWD, and wireline logging) has the ability to collect continuous data sets through the

formations of interest (depending on hole quality). This is particularly important in gas-hydrate-bearing sections, where even with continuous coring programs core recovery is often seriously hampered by the destructive effects of gas exsolution, gas hydrate dissociation and gas expansion during the recovery of non-pressure cores. Borehole log data (generally electrical resistivity data coupled with density/porosity and sonic velocity) is often used to estimate the quantity of gas hydrate within the logged section, but accurate assessment can only come when both the gas hydrate morphology and in situ pore water resistivity profiles are known. The data from pressure coring can provide these important constraints.

Borehole logs are often the first piece of data collected on a gas hydrate expedition, and may be used to direct further coring and sampling. The potential for shallow gas occurrence at or near the base of gas hydrate stability often necessitates the drilling of a pilot hole for safety reasons. This pilot hole may be drilled using LWD tools, serving two ends. Alternatively, once the pilot hole is drilled, wireline logging tools may be deployed in the pilot hole. It is normally the interpretation of these continuous logging data sets that determines if an adjacent coring/testing hole is justified and if so what the best coring/testing strategy in the hole might be. Interpreting downhole logs in gas hydrate bearing formations has been the subject of numerous publications [22-27] which have all shown that downhole geophysical logs can yield information about the presence of gas hydrate.

Electrical resistivity is the borehole data set most often used to infer the presence of gas hydrate, and the only one to be used quantitatively. Elevated downhole electrical resistivity measurements can be used as a reliable indicator of gas hydrate in sediments when the other logs (e.g. gamma) show no other significant lithological changes. Resistivity increases significantly when gas hydrate is present in the formation (as with oil and gas) because it is essentially nonconductive. The traditional method of estimating the saturation of gas hydrate in a formation is to assume that the hydrate has a “pore-filling” morphology and use the well-known Archie relationship (e.g., [22-27]).

If there is no evidence for gas hydrate veins, layers, or other grain-displacing gas hydrate structures, the Archie relationship can be used with some confidence. Assigning the appropriate

Archie's relation parameters can be difficult; this is particularly true in fine-grained sediments, and small differences in these parameters can lead to large differences in the calculated hydrate saturation values [21]. Pressure core gas hydrate saturations can be used to constrain these values. Using pressure core data as spot ground-truth for gas hydrate saturation calculated using electrical resistivity data, the Archie's relation parameters can be adjusted so that the pressure core analysis aligns with the interpreted log data.

When gas hydrate occurs in fine-grained sediments with a complex vein morphology [4, 6, 10] then clearly the simple Archie relationship, which assumes a homogenous matrix, cannot be valid. A dense vein network seen off India, with gas hydrate saturation near 20% by pore volume, corresponded to resistivity values over 100 ohm-m [4]. Even a small number of such electrically-resistive gas hydrate veins within the formation, which might account for less than a percent of gas hydrate by volume, could increase the measured resistivity. This effect can lead to serious overestimates of gas hydrate saturation within a formation, and a simple empirical adjustment to the data is not possible as the underlying model is no longer applicable.

Even when gas hydrate does occur within the pore space, the accurate calculation of gas hydrate saturation requires not only the correct Archie's relation parameters but it also requires the correct background or baseline resistivity profile. As has been noted in the description of porewater freshening analysis, it is not unusual to find significant gradients in the downhole salinity/chlorinity profiles, which further compound the problem of assessing gas hydrate saturations from borehole log data alone. It is ironic that this parameter is required for quantitative gas hydrate estimation in both electrical resistivity and porewater freshening analysis. Analysis of even a small number of pressure cores (5 or 6) within a 200 or 300 meter borehole can be sufficient to constrain the porewater salinity/resistivity to remove this uncertainty from the calculations.

CONCLUSIONS

Gas hydrate detection, and the quantification of its nature, distribution and concentration, involves the use of different observation and measurement techniques to provide "multiple lines of evidence" for the occurrence, morphology and quantification of gas hydrate within a sediment formation. Borehole logging provides continuous data but is

difficult to interpret and quantify in a gas hydrate environment, without ground-truth data concerning both the quantity and geometry of gas hydrate within the sediment. Both infrared thermal analysis and porewater freshening analysis require ground-truth of gas hydrate concentration. The only way to directly and accurately determine the in situ concentration and morphology of gas hydrate in the sediment is to retrieve cores that are sealed immediately after the coring process and recovered to the surface without any loss of the constituents. The analysis of these pressure cores provides the keystone which holds together, calibrates and validates the measurements made by other techniques. Carefully-planned spot pressure coring in an integrated gas hydrate investigation can be used in conjunction with the other data to provide accurate and near continuous data on the nature, morphology, and concentration of gas hydrate throughout the hydrate stability zone.

ACKNOWLEDGEMENTS

We would like to thank all the people that made the collection and analysis of pressure cores possible. This includes our colleagues at Fugro and Geotek (past present and temporary) and the scientists and crews on all the various expeditions especially on the JOIDES Resolution and the Bavenit. We thank the different national and international funding organizations behind the gas hydrate expeditions for enabling this work to take place. We are especially grateful to Tim Collett at the USGS and the US Department of Energy for practical collaboration and financial support on a number of projects.

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