METHANE HYDRATE FORMATION AND DISSOCIATION IN FINE SANDS AT TEMPERATURES NEAR 0°C

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Abstract

In 1996, Canadian and Russian scientists collaborated to construct a laboratory test cell for producing artificially hydrated sediments. This paper presents results from an initial suite of experiments characterizing the formation and dissociation of methane hydrate in fine-grained sand at temperatures near 0°C. Results indicate that P/T equilibrium conditions for hydrate stability in sand are slightly offset from values determined for pure-system hydrates, presumably due to porous media effects. Analyses of P/T response and measurement of gas yields suggest hydration efficiencies approaching 75%, with typical gas yields between 100-150 cm^3/g of soil water. Time series measurements reveal the complexity of hydrate formation/dissociation in natural soil media, with hydrate formation occurring over relatively long periods, while dissociation typically is more rapid. Multiple cycles of hydrate formation, freezing, thawing and dissociation suggest considerable influences arising from changes in soil structure and water memory effects.

Introduction

Gas hydrates are ice-like solids in which water molecules form a crystalline lattice made up of many cavities (or cages) occupied by guest molecules of certain gases. This clathrate structure forms under conditions of relatively high pressure and cold temperature, and permits much greater quantities of gas to be present in soil pore spaces than would be possible if the gas were in its free state. A unit volume of methane hydrate may contain up to 164 volumes of extractable methane gas (Yakushev and Collett, 1992). Globally, methane hydrate deposits are known to occur in offshore sediments overlain by cold, deep water and in association with onshore occurrences of thick permafrost. In recent years a number of research projects have investigated marine occurrences of gas hydrates, with extensive drilling and geophysical studies supported by the Ocean Drilling Project (Kapitan-White, 1996). Limited field studies in permafrost regions generally have been related to hydrocarbon exploration (Collett, 1993a; Judge, 1992; Yakushev and Collett, 1992). Since most geophysical techniques do not discriminate between hydrate-saturated and ice-saturated sediments, these studies typically focus on hydrates occurring beneath the base of ice-bonded permafrost. The first well-documented hydrate samples from within ice-bonded permafrost were taken from a 450 m deep corehole in the Mackenzie Delta (Dallimore and Collett, 1995; Dallimore and Collett, 1998), with samples containing visible lenses of methane hydrate as well as pore space hydrate.

Given that it is almost impossible to recover natural core samples at in situ pressure and temperature conditions, laboratory experiments provide a means for investigating hydrate occurrences in porous soil media under controlled conditions. Such experiments serve to promote an understanding of the physical properties, stability, and kinetics of formation and dissociation of gas hydrates in a range of natural sediments, including the effects of ice on hydrate occurrences in soils at negative temperatures. This paper summarizes a suite of experiments designed to investigate the formation/dissociation characteristics and the physical properties of methane hydrate in fine-grained natural sands, at temperatures near 0°C. Additional details of the experiments are presented in Wright et al. (1998).

Cell description and test procedures

A new gas hydrate test cell, based on an original Russian design (Ershov and Yakushev, 1992), was developed to study formation and dissociation characteristics of natural gas hydrates in porous media. High precision thermistors and pressure transducers permit continuous recording of pressure-temperature (P/T) conditions within the cell, providing insight into the kinetics of hydrate formation and dissociation, including heat transfer characteristics, rates of gas consumption and release, and P/T equilibrium thresholds. A soil sample is exposed to high-pressure gas within the body of the cell (the free gas volume). There is no mechanical loading of the sample. This "passive" system permits experiments to be conducted on relatively undisturbed
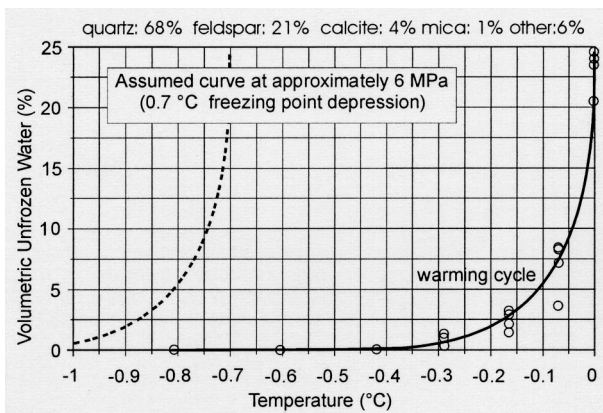
Figure 1. TDR-determined unfrozen water content curve for the test sand.

Figure 2. Pressure-temperature history of the 1st cycle of hydrate formation and dissociation for experiment GSC96-1.

natural soils, as well as on remoulded porous soil media.

A fine-grained natural sand was sieved and washed to obtain a narrow grain-size fraction between 0.125 mm and 0.250 mm, with an approximate mineralogical composition of 68% quartz, 21% feldspar, 4% calcite, less than 1% mica and about 6% other minerals. Time Domain Reflectometry (TDR) was employed to determine a temperature-dependent unfrozen water content curve for the soil (Figure 1, thaw cycle of previously frozen soil). At atmospheric pressures, virtually no unfrozen soil water remained below -0.3°C. The dashed line presents an adjusted curve reflecting a mainly pressure-induced freezing-point depression observed in the experiments. Soil porosity targets were between 39-43%, and gravimetric water content either 17% or 20%, yielding pore saturation levels of 60-80%. The unsaturated condition promotes relatively unrestricted pathways for penetration of the hydrate-forming gas into interior pore spaces.

The cell was purged of air and charged with methane gas (> 99.997 % pure) to a pressure of approximately 8 MPa, after which the cell was hermetically sealed. Pressure (P) and temperature (T) conditions within the free gas volume, and the temperature of the interior of the soil sample, were continuously recorded during the course of the experiment.

Results

INTERPRETATION OF PRESSURE-TEMPERATURE (1ST-CYCLE OBSERVATIONS)

Figure 2 presents the P/T history for the first 100 hours of experiment GSC96-1, and forms the basis for discussion. Initial P/T conditions were outside the stability envelope for methane hydrate. During cooling towards a target temperature of about +3°C, cell pressure and temperature decreased in accordance with the general gas laws, permitting determination of the expected pressure response to changing cell tempera-
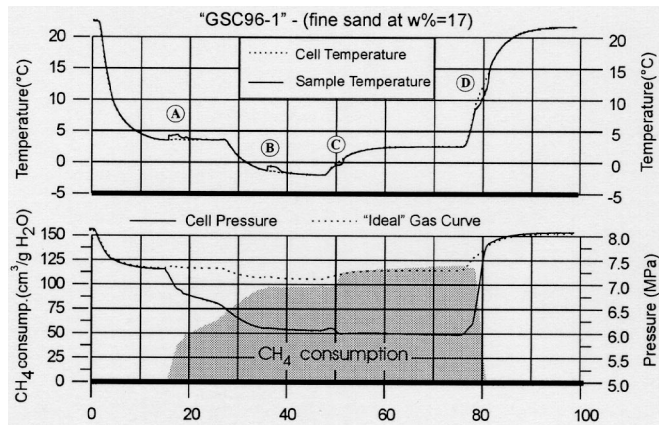
ture (dashed pressure curve in Figure 2). Beyond A, the decrease in cell pressure was greater than could be accounted for by changes in temperature alone, indicating the incorporation of methane gas into hydrate. This conclusion is supported by an increase in sample temperature attributed to the release of heat during the formation of methane hydrate (presented as the equivalent volume of methane incorporated per gram of soil water). Theoretically, complete integration of 1 gram of water into Structure I hydrate consumes approximately $205 cm^3$ of methane (after Yakushev and Collett, 1992).

Sample temperature initially increased sharply at A, maintaining a measurable temperature difference between the sample and the free gas volume for about 10 hours (hr.15- hr.25). The average CH_4 consumption rate during this period was approximately 5 cm^3/h per gram of soil water. A second stage of cooling was initiated with a target temperature of -5°C. Approaching B, cell temperature decreased below 0°C, with a corresponding reduction in cell pressure. However, the sharp increase in sample temperature at B occurred without a coincident drop in cell pressure as was observed at A. This is interpreted as a release of latent heat during freezing of the remaining soil pore water, with CH_4 consumption dropping abruptly to about 0.1 cm^3/h/g H_2O. Total CH_4 consumed at this point was nearly 100 cm^3/g H_2O. Significant sub-cooling was observed, followed by a freezing-point depression of about 0.7°C (attributed primarily to the elevated pressure). This latent heat effect persisted strongly for approximately 4 hours, with sample temperature remaining about 2°C higher than that of the free gas volume (cell temperature).

Thawing was initiated at t = 47 hours, and cell temperature increased to about +3°C in approximately 15 hours. At C, ice formed at B began to melt, absorbing heat from the surrounding soil matrix and reducing sample temperature relative to that of the cell. As was

the case during sample freezing, a temperature plateau occurred at approximately -0.7°C, persisting for about 3 hours. Cell pressure initially increased in response to the increasing cell temperature, but beyond C, pressures decreased despite steadily increasing temperature, indicating renewed consumption of methane gas. The rate of CH_4 consumption exceeded $5 cm^3/h/g$ H_2O during the period of ice melting and was accompanied by a reduction of sample temperature relative to the free gas volume.

Further warming returned the system to initial pressure and temperature conditions (Figure 2). Initially, cell temperature increased sharply, with cell pressure increasing even though CH_4 consumption continued. At D, methane consumption ceased and hydrate began to dissociate. The coincident release of methane into the free gas volume resulted in sharply increased cell pressure, and sample temperature lagged that of the cell, being as much as 2.5°C cooler during the dissociation stage. Hydrate dissociation progressed rapidly in comparison to hydrate formation, with complete dissociation occurring in about 3 hours. CH_4 release rates were about 40 cm^3/h per gram of soil water. Approximately 20 hours later the system had restabilized at initial P/T conditions, confirming that no gas had been lost from the test cell through leakage.

PHYSICAL TESTING OF HYDRATED SOIL SAMPLES

Experiments were terminated at the end of the second or third freezing cycle. Hydrated soil samples were found to be stable throughout the sampling period (typically, up to several hours) when stored at negative temperatures (about -8°C) and atmospheric pressure. This metastable behaviour has been called the self-preservation effect (Ershov and Yakushev, 1992) and is thought to be due to the formation of a thin ice shell on the surfaces of the hydrate following depressurization. Samples were generally well-bonded in the self-preserved state, and were sectioned to produce a number of disk-shaped subsamples, 1-2 cm in thickness. Binocular microscopy at 50x to 100x magnification revealed that virtually all of the hydrate occurred within pore spaces (i.e., no visible, massive hydrate). Typically, one half of each disk was used for measurements of soil bulk density and water content, and the other dissociated to determine the volume of methane gas released (estimated by fluid displacement method).

Figure 3 summarizes physical properties and gas yields of the subsamples tested. Methane gas yield within the sample was found to strongly reflect the distribution of pore water, ranging from about $10 cm^3/g$ to $23 cm^3/g$ of hydrated soil material. The degree of pore-filling by hydrate for GSC96-1 ranged from a minimum of 0.45 to a high of 0.63, with an average of 0.55 for all
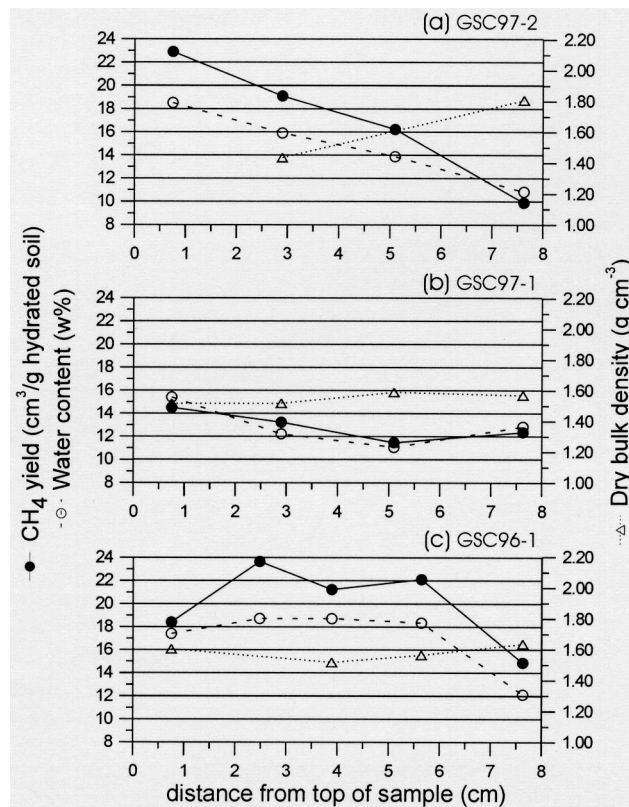

Figure 3. Summary of physical properties testing and gas yield measurements for subsamples from three experiments.

subsamples, based on a specific volume of 1.26 for water incorporated into methane hydrate (Makogon, 1981).

Table 1 describes bulk sample characteristics for each experiment. Pro-rated gas yield figures assume that each subsample is representative of the larger section of the bulk sample from which it was taken, and are presented as the volume of methane released per gram of soil water. Pro-rated gas yields were used to reconcile calculated methane gas consumption figures with measured gas yields (yield/consumption ratio), and as a measure of hydration efficiency (percent of maximum yield if all water were integrated into the clathrate structure).

Calculated hydrate efficiencies ranged between 49% and 72% at opposite extremes of the sample, and surprisingly also reflected the distribution of water. One might expect hydration efficiencies to increase as water content decreases, since lower water content implies a relative increase in the surface-to-volume ratio of water in contact with methane gas. However, this same condition may lead to greater surface area of hydrate exposed to atmospheric pressures upon opening of the cell. Because of the high surface to volume ratio, a greater proportion of the hydrate mass dissociates immediately to form the protective ice film characteristic of the self-preservation phenomenon. Reduced methane yields upon sampling of the specimen would

Table 1. Physical characteristics and gas yield of bulk samples

	GSC96-1	GSC97-1	GSC97-2
Initial w% target	17%	17%	20%
Mass of sample (g)	245.9	225.1	228.0
Sample volume (cm³)	135.3	133.1	136.5
Bulk density (g/cm³)	1.82	1.69	1.67
Pro-rated methane yield (cm³) [1]	4932	2902	3883
Avg. Hydration Efficiency	67%	55%	63%
Predicted cap hydrate yield (cm³)	-	820	-
Predicted snowy hydrate yield (cm³)	148	919	740
Estimated total yield (cm³)	5080	4641	4623
Methane consumption (from P/T data)	4685	4963	5346
Yield/Consumption Ratio	1.08	0.94	0.86

[1] based on mean gas yield per gram of soil water (average of subsamples), multiplied by an estimate of the mass of sample water remaining in soil pore spaces at the end of the experiment

falsely indicate a reduced hydration efficiency relative to the condition existing prior to cell depressurization.

Discussion and conclusion

INITIAL HYDRATE FORMATION AT POSITIVE TEMPERATURES

Figure 4 summarizes CH_4 consumption (hydrate growth) at positive temperatures during the first and subsequent cycles of each experiment. Note that the water content for experiments 96-1 and 97-1 was 17%,

Figure 4. Comparison of hydrate formation rates for 1st and subsequent cycles of three experiments.

but was 20% for 97-2. Data reveal several phases of hydrate formation and suggest considerable effects of multiple formation cycles. For the samples at 17% water content (40% porosity, 68% water saturation) a relative abundance of both water and gas in soil pores creates numerous gas/water interfaces favourable for hydrate growth. First-cycle CH_4 consumption rates for 96-1 and 97-1 averaged about $5 cm^3/hr/g$ H_2O during the first 20 hours. Second-cycle rates were much greater ($20 cm^3/h/g$), with total CH_4 consumption exceeding 1st-cycle values within the first 5 hours, followed by a marked decrease to about $0.1 cm^3/hr/g$ H_2O. Calculations of the proportion of soil water incorporated as hydrate indicate that considerable amounts of free water remained, but presumably this water was isolated from methane gas.

Higher formation rates during the second cycle might be explained in terms of the so-called "water memory" effect, whereby large numbers of hydrogen bonds between water molecules persist for some time after dissociation of hydrate or thawing of ice (Pauling, 1945; Makogon, 1981). This water may be relatively predisposed to integration into the clathrate structure in the presence of methane gas. Changes in soil structure, induced by such factors as volume expansion due to hydrate/ice formation, as well as a more favourable gas-water distribution following dissociation of hydrate formed in the initial cycle, may also contribute to enhanced 2nd-cycle formation rates. However, CH_4 consumption rates during 2nd and subsequent cycles typically decrease abruptly soon after an initial stage of rapid hydrate growth. This suggests that a supply limi-
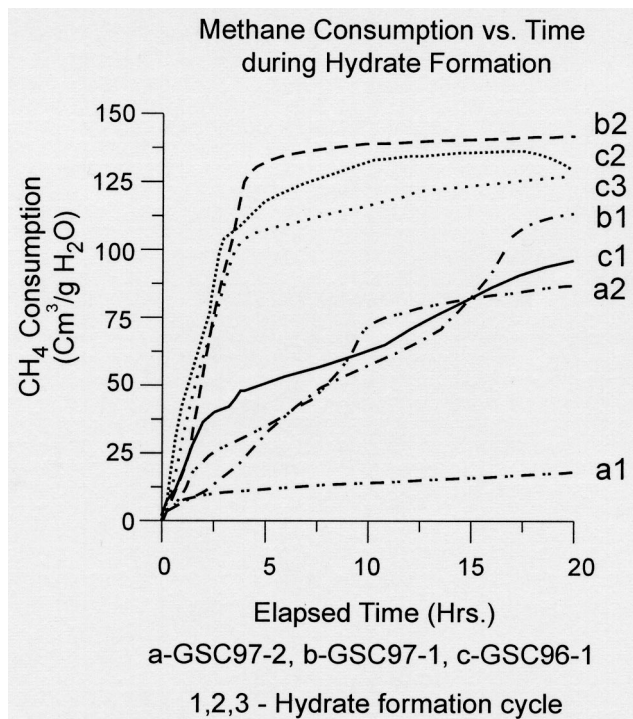
ted situation exists with respect to CH_4 availability at hydrate formation interfaces.

Hydrate formation characteristics in 97-2 were similar but formation rates and total hydrate produced were lower, particularly during the 1st cycle. This is attributed to higher pore-water saturation (80%) which implies a less favourable initial distribution of gas and water. This situation may also promote more rapid clogging of CH_4 transport pathways with growing hydrate crystals.

HYDRATE AND PORE ICE FORMATION AT NEGATIVE TEMPERATURES

In contrast to the generally strong latent heat effect observed during 1st-cycle freeze stages, latent heat releases during subsequent freeze stages were of shorter duration (< 1 hr.), indicating less free water available to form ice. This implies that more water was integrated into hydrate during subsequent cycles relative to the 1st. This is confirmed by higher total CH_4 consumption at the initiation of the 2nd and 3rd freeze cycles in 96-1 (about 137 compared to $100 cm^3/g H_2O$).

Data suggest low but continuous CH_4 consumption during the freeze stage of all experiments. Note that Figure 1 indicates that less than 1.0% of water in the samples remains unfrozen at temperatures below -1.0°C, even after accounting for a pressure induced freezing-point depression, and it is uncertain if this water is available for continued hydrate growth. We might consider that hydrate forms directly from pore ice during this stage. Mechanisms have been proposed in which relatively mobile water molecules at the outer boundaries of ice crystals, in the presence of a hydrate-forming gas, reorient into partial and subsequently complete hydrate cage structures (Sloan, 1990). These mechanisms may play a significant role in the generation of gas hydrate occurrences in some high Arctic permafrost settings.

HYDRATE FORMATION DURING THAWING OF PORE ICE

The rate of CH_4 consumption and amount of hydrate formed during the thaw stage varied between experiments. Where high rates of formation were interrupted by freezing (1st cycle, 96-1), upon thawing, formation resumed at comparable or higher rates. Where formation rates and total CH_4 consumption were comparatively low, post-thaw formation rates increased substantially. Water memory effects may contribute significantly to the increased rates of formation observed during the thaw stage. Widening of some pore space pathways due to the volumetric expansion of ice may accommodate the redistribution of gas and water in pore spaces as thawing progresses, creating additional gas/water interfaces for renewed hydrate growth.

The apparent contradiction presented by decreasing sample temperatures during hydrate formation as pore ice thaws (Figure 2, at C), can be explained if we consider that heat is absorbed as ice melts, while the formation of hydrate releases heat. Since a net cooling of the sample was observed (relative to cell temperature), we can conclude that only a fraction of the water made available during thawing was converted to hydrate immediately.

MULTIPLE CYCLES OF HYDRATE FORMATION AND DISSOCIATION

It is well known from laboratory experiments that multiple freeze-thaw cycles can induce considerable fluctuations in kinetic processes in natural sediments. The influence of multiple cycles on rates of hydrate formation was discussed earlier in this paper. Pressure and temperature conditions at initiation of hydrate growth also appear to be influenced by cycling. P/T data points plotted in Figure 5 were taken from the three experiments described in this paper, and also from two additional experiments. The data are widely scattered, though all are shifted to the left of the methane hydrate equilibrium curve determined for pure water-methane systems. In general, the amount of subcooling required to initiate hydrate growth in 2nd and subsequent cycles is considerably less than that of the 1st cycle. Makogon (1981) suggests this difference is due to the presence of relatively high numbers of hydrogen-bonded water molecules present following 1st-cycle hydrate dissociation, which reduces the amount of subcooling required to initiate nucleation. Also note that the amount of 1st-cycle sub-cooling is generally much greater than the
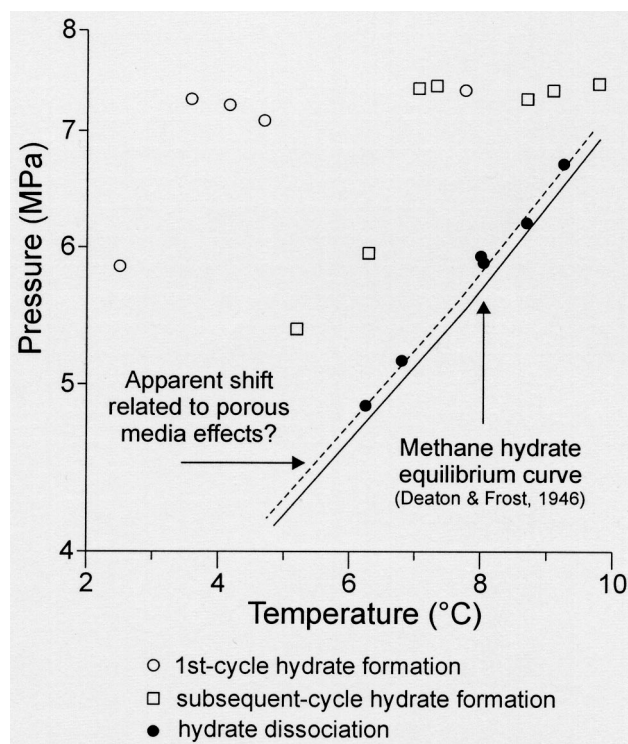

Figure 5. Pressure-temperature conditions at initiation of hydrate formation and dissociation.

optimum of 2-3°C suggested for pure gas-water systems (Makogan, 1981; Sloan, 1990). We speculate that some of this additional sub-cooling may be related to surface effects of the porous soil medium.

In contrast, dissociation rates for different experiments and successive cycles were remarkably uniform, with complete dissociation generally occurring within a few hours. This is presumably because hydrate dissociation was driven by a strong temperature forcing, and was not limited by the permeability characteristics of the soil. In the case of very subtle forcing (by either increasing temperature or decreasing pressure), dissociation rates are likely to be limited by local cooling effects and pressure increase as dissociation proceeds, tending to shift P/T conditions back into the stability envelope. This effect should be more apparent in finer-grained soils having lower permeability to gas and water flows.

INFLUENCE OF THE POROUS MEDIUM ON THE P/T EQUILIBRIUM THRESHOLD

In contrast, data describing P/T conditions at the initiation of hydrate dissociation are not influenced by sub-cooling and nucleation effects, and display little scatter (Figure 5). A slight shift to the left of the methane hydrate equilibrium curve for pure systems is apparent. Because the shift is small, it is difficult to infer a cause-effect relation with respect to the porous soil medium. However, if we consider that the data points for hydrate dissociation describe an alternative equilibrium curve specific to the water-gas-soil system, then we have observed a shift in the hydrate stability threshold from that determined for systems involving water and methane only. This shift implies that additional heat must be removed from the system (at a given pressure) in order to initiate hydrate formation. This is similar to the freezing-point depression observed as a porous media effect in fine-grained soils. Planned future experiments using finer-grained soil materials should clarify this issue.

Summary

The development of a simple Gas Hydrate Test Cell has facilitated laboratory investigations into the P/T conditions and kinetics of natural gas hydrate formation and dissociation in fine-grained natural sands. A small but measurable shift observed in the P/T equilibrium threshold during hydrate dissociation may be related to weakly-bound water in association with soil particle surfaces in unsaturated fine sands. Continuous recording of pressure-temperature histories, physical properties testing and gas yield measurements of hydrated soil samples provide insights into the factors influencing rates of hydrate formation and dissociation, and which impose practical limits on the hydrate pore-occupancy achievable in the laboratory.

The rate and duration of hydrate growth in any particular stage depends on the physical characteristics of the soil medium (grain-size, porosity, water content) and at laboratory time scales at least, on the history of hydrate formation/dissociation and water memory effects. These same factors ultimately determine the degree of soil pore-filling by hydrate, especially as related to initial pore water saturation levels, and its impact on the efficiency of gas-water transport. Freezing of soil pore water greatly reduces, but does not halt the progression of hydrate growth. At geologic time-scales, it is likely that this phenomenon (and other very slow processes such as diffusion of gas through water and ice) plays a major role in determining the characteristics of gas hydrate occurrences in natural settings.

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