

An Experimental Study of Gas Hydrate and Ice Accumulation in Sediments

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ABSTRACT

Experimental results on hydrate and ice formation conditions in the pores of sandy sediments during temperature cycles are presented. To better understand how hydrate accumulates in sandy sediments, we measured the accumulation of CH₄ and CO₂ hydrate and ice in sandy sediments under various conditions. With the pressure above that needed for hydrate formation, cycling the temperature below and above the freezing point of water increased the amount of hydrate in the sediments. The self-preservation effect allowed us to determine the structure and some physical properties of these sediments that contained ice and hydrate.

KEY WORDS: Gas hydrate; ice; hydrate formation; freezing; sand; CO₂; methane.

INTRODUCTION

Frozen sediments exist on polar shelves under seawater. Such sediments occur in various areas of the Arctic shelf including areas in the Barents Sea, Kara Sea, Laptev Sea, and Beaufort Sea (Romanovskii, 1993). Measurements, aided by calculations, show that their thicknesses are tens to hundreds of meters. Geophysical data, including gas emissions during drilling, outgassing of cores, and gas fountains indicate that such sediment includes gas hydrates (Ginsburg and Soloviev, 1998; Melnikov and Spesivzev, 1995; Collett and Dallimore, 2000). Geological studies and thermal modeling of undersea conditions indicate that ice and gas hydrates can form in sediments when the environmental temperature is lowered (Romanovskii, 1993; Collett and Dallimore, 2000).

The existence of sediment regions containing ice and gas hydrates on a polar shelf significantly complicate the exploration of large gas deposits, which was discovered not long ago on a polar ice shelf. For such explorations, research on the formation, existence, and properties of frozen gas hydrates in sediments is needed. In particular, laboratory experiments on gas hydrates and ice formation in sediments is necessary.

There have been recent experiments on hydrate formation in sediments. Such experiments have shown that the conditions of gas

hydrate formation in the pores of sediments differ from those without sediments. In sediments, the phase equilibrium conditions, hereafter P/T conditions shift to lower temperatures and higher pressures. This shows that mineral particle surfaces and the pores in sediments affect the phase transitions of water and gas into gas hydrates and ice (e.g., Chuvilin et al., 2000; Wright et al., 1999). Gas hydrates, both with and without sediments, are metastable below 0 °C (273K) because the gas hydrate self-preservation effect allows them to exist for long periods of time in nonequilibrium P/T conditions (e.g., Ershov et al., 1991; Takeya et al., 2001). However, the formation of gas hydrates in sediments remains poorly known; in particular, the amount and properties of hydrates in pores is not well understood.

This paper describes an experimental study of gas hydrate and ice accumulation in sandy sediments that experience various temperature cycles.

PROCEDURES

Experiments were done using a special pressure chamber built in AIST, Sapporo. This chamber had pressure and temperature sensors that were connected to a recording system. The chamber was equipped with a special jacket connected to a HAAKE model N8 circulating cooler for cooling the test sample during the experiments.

Fine-grained, natural quartz sand and sand mixtures with 7% montmorillonite clay were used in the experiments, but most experiments used sand (Table 1).

Table 1. Grain size and composition of the soils in the experiments.

Sediment type	Grain size distribution, %					
	Grain size, mm					
	>2	2-1	1-0,5	0,5-0,25	0,25-0,01	<0,01
Quartz sand	-	-	1,37	74,14	24,34	0,15

The soil samples were cylindrical with a diameter of either 7.3 cm or 6.4 cm and lengths of about 13.0-13.5 cm. Samples were prepared in a cylindrical Plexiglas container using a layer-by-layer consolidation method. The container with the soil sample was loaded into the chamber. We tried to make samples with soil porosity of 40 - 50% and

gravimetric water content of 14 - 17%, which would result in pore saturation levels of 40 - 55%. Unsaturated pores allow the hydrate gases to penetrate into interior pore spaces. Two hydrate forming gases, CH₄ and CO₂, were used in the experiments.

After assembling the chamber with the sample inside, the cell was purged of air and filled with either CH₄ or CO₂ gas. If CH₄ was used, the pressure inside the chamber was 8 - 9 MPa; if CO₂ was used, the pressure inside the chamber was 3.5 - 4.0 MPa.

During an experiment, the pressurized chamber with sample was gradually cooled and heated to temperatures between -10 and +20 °C. Decrease of temperature in the chamber below the equilibrium hydrate temperature (P/T point) caused gas hydrate formation. Further decrease of temperature below 0 °C caused ice formation. The composition of hydrate, gas, and ice or water was determined by the temperature and the pressure. Each experiment finished when the temperature reached -10 °C; at this temperature, the sample was completely frozen. Then, the pressure inside the chamber was reduced to atmospheric pressure, and samples were removed in the cold room at -10 °C. The samples were stable due to the self-preservation effect of the ice; hence we could study the sample structure changes that occurred during hydrate and ice formation (Chuvilin and Yakushev, 1998). Recovered hydrate-containing samples were described, cut into 6 pieces, then the density, and the water, gas, and hydrate content of each piece were determined. Hydrate content in the samples was measured by the weight changes of sample before and after the experiment, and also from gas content data.

RESULTS

Kinetics and P/T condition of hydrate and ice formation in the samples

The study of pressure and temperature changes with time allowed us to determine when and what type of water phase transition occurred within the samples. In all experiments, the temperature-pressure curves were qualitatively the same. Hydrate always formed when the sand samples were initially saturated with gas. Furthermore, ice always formed when the temperature decreased below 0 °C. When the sediment is heated slightly above the ice melting temperature, the melt water can contact the gas and form hydrate, which is known as secondary hydrate formation (Chuvilin et al., 1999). Upon further heating above the P/T temperature, the hydrates will decompose. Figure 1 has typical experimental curves of P/T conditions for methane-saturated sand samples.

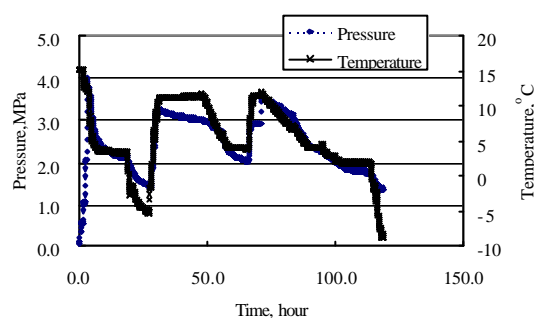


Figure 1. Kinetic curve showing changes of P/T conditions for experiment with CO₂ saturated sand sample (Win=17%).

Table 2 lists the experimental data of P/T condition of CO₂ and CH₄ hydrate formation in the sandy samples.

Table 2. P/T conditions of gas hydrate formation in the sandy samples.

Soil type	T _{exp} , °C	ΔT, °C	P _{exp} , MPa	ΔP, MPa
CO ₂ gas hydrate				
Sand (Win=17)	8,0	0,3	3,4	0,1
	8,1	0,2	3,4	0,05
	8,0	0,3	3,4	0,1
	8,1	0,2	3,4	0,05
	8,0	0,3	3,6	0,3
	8,1	0,2	3,6	0,25
	7,3	0,2	3,1	0,2
	7,25	0,2	3,1	0,2
Sand (Win=14%)	7,75	0,5	3,4	0,25
	7,9	0,3	3,4	0,2
	8,0	0,3	3,4	0,1
Sand with 7% montmorillonite (Win=17%)	7,75	0,6	3,5	0,35
	7,2	1,1	3,5	0,5
CH ₄ gas hydrate				
Sand (Win=17%)	9,35	3,9	8,3	1,6
	9,5	3,6	8,3	1,5
	9,35	3,9	8,3	1,6
	9,5	3,6	8,3	1,5

The data show that hydrate formation conditions in the wet, sandy sediment have shifted to higher pressures and lower temperatures the equilibrium values for free-water plus hydrate forming gas. The CO₂-saturated samples have smaller deviations in experimental P/T values of hydrate formation (ΔT, ΔP) than the CH₄ saturated samples; for example, CH₄ saturated samples have maximum ΔT of 3.6 - 3.9 °C and maximum ΔP of 1.6 MPa, whereas the corresponding maximum deviation for CO₂ saturated samples are 1.1 °C and 0.5 MPa. These small deviations occurred even in samples containing clay particles where water channels are more connected and deep supercooling is necessary to convert it into hydrate structure.

Only some of the pore water was converted into hydrate during cooling of the sediment; the remaining water froze into ice during freezing. The freezing temperature of this water depends on its quantity, the pore space, and the gas pressure (Chuvilin et al., 2000). The data in Table 3 shows how this freezing temperature depends on gas pressure and sediment type for both CO₂ and CH₄ gas.

Table 3. Freezing temperature of remaining water in sandy sample under gas pressure.

Number of test	Number of cooling cycle	Pressure (P), MPa	Temperature (T), °C	T /P, °C/MPa
CO ₂ gas pressure				
A1, sand (Win=17%)	1	2,11	-1,5	0,71
	2	1,83	-1,5	0,82
A3, sand (Win=17%)	1	1,76	-1,35	0,77
	2	1,54	-1,35	0,90
A4, sand (Win=14%)	1	2,05	-1,35	0,66
	2	1,55	-1,45	0,94
A5, sand with 7% montmorillonite (Win=17,3%)	1	2,4	-2,35	0,98
	3	2,4	-2,7	1,13
	4	2,05	-2,6	1,27
	5	1,85	-3,0	1,62
	6	1,7	-3,0	1,76
CH ₄ gas pressure				
A6, sand (Win=15,1%)	1	5,75	-0,45	0,08
	2	3,75	-0,45	0,12
	4	7,07	-0,85	0,12

During the thawing of sediments containing ice and hydrate, additional hydrates can form if the pressure is above the equilibrium pressure (Chuvilin et al., 1999). In our experiments, such hydrate formation is indicated by the pressure decrease after some of the ice melts (Fig 2).

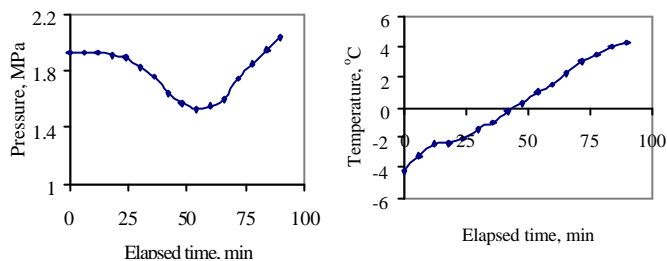


Figure 2. Decrease of gas pressure in chamber during the thaw of sample with frozen CO₂ hydrate and sand with 7% montmorillonite clay (W=17%).

The pressure decrease during secondary gas hydrate formation was 0,4 MPa or less. Because the final pressure is still above the equilibrium pressure, additional hydrate formation in sediments could occur in subsequent freeze-thaw cycles.

Structure and physical properties of sediments with ice and hydrate

Each sample was analyzed after removal from the chamber. All samples were characterized as having a massive cryohydrate structure. Porphyry-like ice-hydrate inclusions, which did not exceed a few millimeters, were rare. Figure 3 shows typical structures of the samples. Hydrate and ice accumulated in the pore space of the sediments and formed porous hydrate-ice-cement.

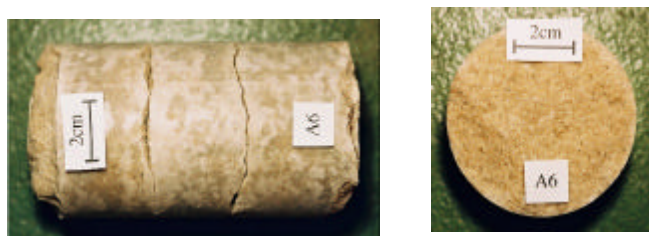


Figure 3. Structure of a sand sample that contains ice and hydrate (test 6A, volumetric CH₄ hydrate content 17,3%, volumetric ice content 6,4%).

The weights of the samples, the sample densities, and the degree of pore filling all increased by the experimental procedure. The determination of hydrate and ice accumulation in the sandy samples show that up to 70% of the initial pore water was transformed to hydrate during the experiments (Table 4).

Table 4. Average value of gas hydrate and ice accumulation in the sandy samples.

Test No.	Condition of test	Gas hydrate content, %		Ice content, %		Hydrate ratio
		Gravi-metric	Volu-metric	Gravi-metric	Volu-metric	
CO2 gas hydrate accumulation						
A3	Sand, W-17%, $\rho_d = 1,44\text{g/cm}^3$	8,7	11,2	10,1	15,6	0,38
A4	Sand, W-14%, $\rho_d = 1,42\text{g/cm}^3$	13,0	16,9	5,1	7,9	0,66
CH4 gas hydrate accumulation						
A6	Sand, W-15,1%, $\rho_d = 1,42\text{g/cm}^3$	12,1	17,3	4,6	6,4	0,67
A7	Sand, W-17%, $\rho_d = 1,42 \text{ g/cm}^3$	13,3	20,4	3,7	5,5	0,68

General hydrate content in the samples reached 13% (gravimetric hydrate content) or about 20% from volume of sample (volumetric hydrate content). Some pore water froze when the temperature decreased below 0 °C. At high hydrate contents, the gravimetric ice content was reduced by up to 4-5%. The analysis of the experimental data shows that the gas hydrate content in the pore space of sediments increased due to the temperature cycle near the phase region where water-gas hydrate and water-ice transformations occur. Hence, in test A4, we repeatedly cycled the sample through ice freeze-thaw cycles. The resulting accumulation of CO₂ hydrate was 17%, and the amount of pore water transformed into hydrate (hydrate ratio) was 0,66. In contrast, test sample A3 did not have repeated temperature cycles above and below the phase transitions and the hydrate ratio was only 0.38. This effect from temperature cycles also occurred with CH₄ hydrate samples.

The distribution of gas hydrate in a sample also depends on the conditions of hydrate formation and the temperature distribution in the sample. Figures 4 and 5 show the total water content (ice and water in gas hydrate) and gas hydrate content in CH₄ saturated sand samples after the experiments.

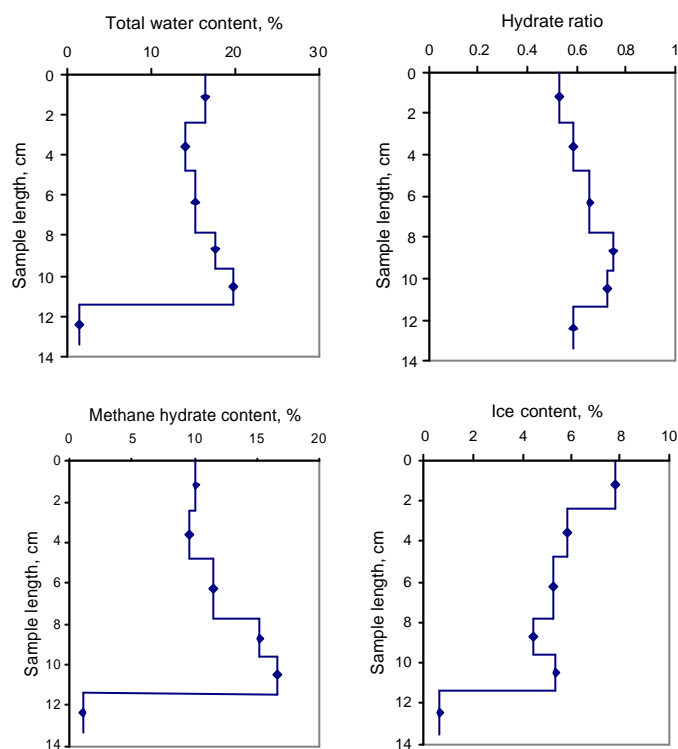


Figure 4. Gravimetric content distribution of total water, total ice content, total methane hydrate content, and hydrate ratio in a sand sample (test A6, W_{in}= 15,1%).

The conditions of cooling in these experiments were different (Fig. 6). During the cooling stage of test A6, the temperature on top and bottom faces were higher than the inside (the region 8-10 cm from the top of sample); thus, the most favorable position for accumulation was in the region 8-10 cm from top of the sample, which is where the temperature was lower. In this part of sample, the accumulation of gas hydrate exceeded 15% and the hydrate ratio increased up to 0,74. In the region of greater hydrate accumulation there was an additional migration of water from the lowermost zone. This lowermost zone was dehydrated;

its total water content was 2% or less. Regions of higher hydrate content tend to be regions of lower ice content and vice-versa; for example, in the region of highest hydrate accumulation, the ice content was 5% or less, whereas the top surface of the sample had an ice content of to 8%.

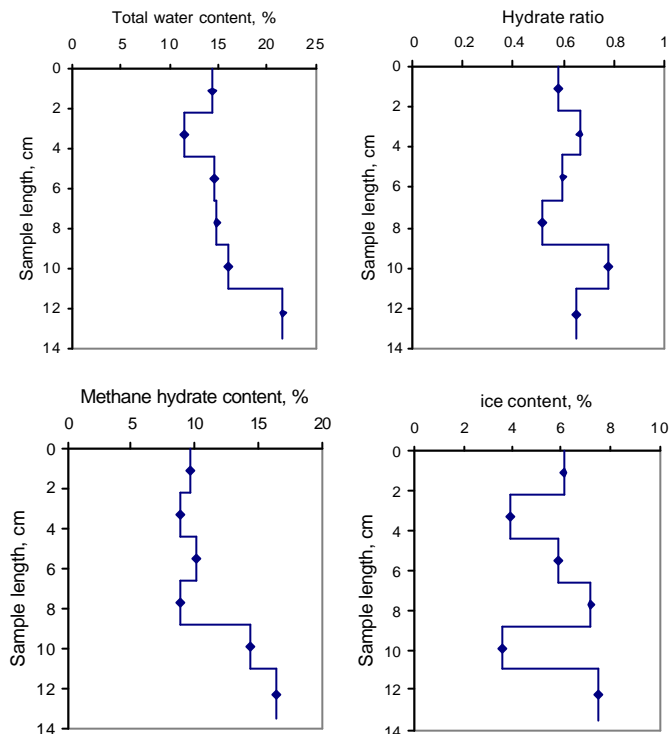


Figure 5. Gravimetric content distribution of total water, total ice content, total methane hydrate content, and hydrate ratio in a sand sample (test A7, Win= 17,0%).

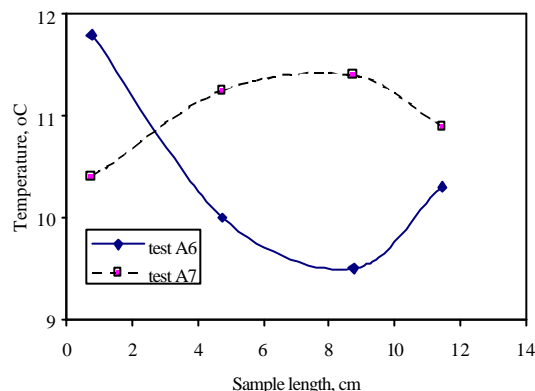


Figure 6. Temperature distributions in test samples A6 and A7 during the 30min cooling period prior to the initial formation of gas hydrates.

In test A7, the temperatures on the top and bottom faces (i.e., on the cooling stage) were lower than those in the inside. This temperature distribution is similar to those in previous experiments (Chuvilin et al 2000). Having lower temperatures and free gas-water contact on the top and bottom surfaces of a sample are favorable conditions for initial hydrate formation. This caused surface gas hydrate accumulation,

which has been called a gas hydrate cap (Ershov et al., 1993; Groisman, 1986; Melnikov and Nesterov, 1997).

The formation of surface gas hydrate accumulation (figure 7) caused some redistribution of the pore water.

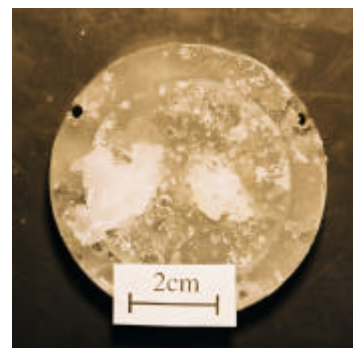


Figure 7. Surface methane hydrate accumulation as a gas hydrate cap on the top plate of the sand sample in test A7.

The face parts here are characterized by their greater total water content. The greatest hydrate accumulation (more than 15%) was fixed in the bottom part of a sample; gravity also causes some water to flow to the bottom. The central region has a fixed, lower hydrate accumulation and thus a lower value of hydrate ratio (0,6 or less). The distribution of ice content over a whole sample is no uniform with variations that range from 4 to 7%. Hence, these results show that the amount of gas hydrate in a sample is correlated with the temperature distribution.

CONCLUSIONS

The experiments in the present study showed that 1) gas hydrates accumulated in the pore space of sediments in significant amounts even without forming inclusions, 2) pore ice-water freeze-thaw temperature cycles increased the hydrate accumulation in the pore space of sediments, and 3) ice formation and hydrate formation affect each other in sediments. Hence, the temperature distribution in a region of sediments can significantly influence the accumulation of hydrate.

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