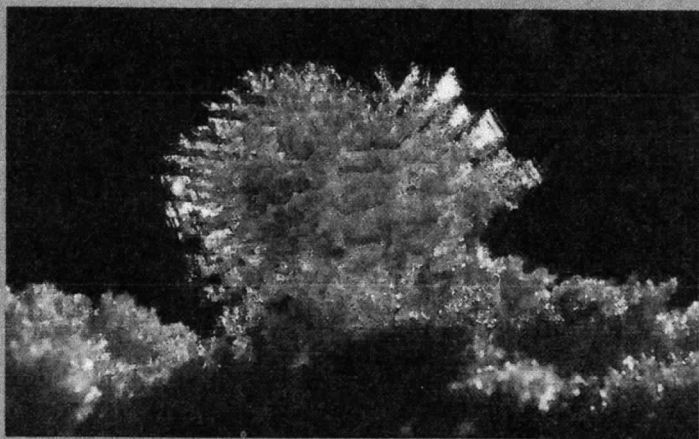K. Hutter Y. Wang H. Beer (Eds.)

Advances in Cold-Region Thermal Engineering and Sciences

Technological, Environmental, and Climatological Impact

Experimental Study of Gas Hydrate Formation in Porous Media

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Abstract. The experimental discovery of gas-hydrate self-preservation phenomenon made it possible to establish gas hydrates as one of the permafrost components such as ice, unfrozen water and gas. However, this component is so far poorly investigated. Little is known about conditions of formation and decomposition of gas hydrates in dispersed rocks. Special experimental chambers are used by the authors for the simulation of hydrate formation/decomposition processes in porous media and the study of different factors influencing the hydrate formation in dispersed rocks. Our experimental research reveals new data on kinetics and P, T- conditions of hydrate formation and decomposition in dispersed rocks. The experimental data show, that the process of hydrate formation in porous media depends on composition and structure of dispersed rocks and also on some external condition.

1 Introduction

Natural gas hydrate formation is a global phenomenon, exceeding the ice formation on the Earth crust. Hydrates are crystalline clathrate compounds of gas and water spread in permafrost regions and in the ocean floor (at water depth below 500 m). Their instability at atmospheric pressure makes their experimental study very difficult, especially in dispersed media. Experimental discovery and field studies of metastable permafrost gas hydrates (about 10 years ago) make it possible to consider gas hydrates as one of the main components of frozen rocks such as unfrozen water, ice and gas (Ershov E. D. et al. [2]). Moreover, discovery of this self-preservation phenomenon, when hydrates exist at non-equilibrium thermodynamic conditions, has opened new possibilities for the experimental study of hydrate-enriched deposits. During the last years the Geocryology Department of the Moscow State University conducted experimental studies targeted to the determination of the clay-particle influence on the process of hydrate-formation within dispersed rocks. This problem has so far not been studied, although there are some theoretical predictions and sporadic experimental data. Sometimes they are in contradiction with each other. For example, Y. Makogon [4] theoretically predicts an increase of the equilibrium hydrate formation pressure when the dispersed rock particle size decreases. S. B. Cha et.al. [1] have experimentally shown the

opposite phenomenon, namely that hydrate formation within a suspension of bentonite in water starts at pressures lower than equilibrium in the system free gas-liquid water. But experimental data of V. Yakushev [9], T. Uchida et al. [7] were in agreement with the theoretical prediction of Y.Makogon.

Unfortunately, data received earlier do not allow us to establish the physical and chemical nature of the described phenomena. Also, there are no data on the influence of clay particles on the micro and macro structure of hydrate-containing sediments during hydrate accumulation; this is very important for the understanding of the origin of natural hydrate textures in sediments. There are many uncertainties in the experimental data on water migration during methane hydrate formation in clays. V. Yakushev [9] reported absence of considerable water transfer during hydrate formation in heavy clays; at the same time, V. P. Melnikov and A. N. Nesterov [5] observed a thick propane hydrate rim on the top surface of the water-enriched heavy clay.

In this work we study the influence of different contents of clay particles on the phase equilibrium, water transfer and structure changes in the course of methane-hydrate formation in fine-grained quartz sand.

2   Procedure

2.1   Experimental equipment

The experimental chamber constructed jointly with researchers from the Geological Survey of Canada (F.Wright et al. [8]), was used for the hydrate formation and the study in the soil samples. This high pressure chamber, made of stainless steel, was equipped by a manometer, pressure and temperature sensors and valves for gas injection and withdrawal. Its general construction is the same as described in the paper of Ershov E.D. and Yakushev V.S. [3]. P-, T- data are recorded by a data logger and transmitted to a computer in accordance with the time step. Data documentation was controlled by "Sciemetric" software.

The experimental equipment included a cold room (temperature down to - 10°C), a methane cylinder (pressure 15 MPa, 99,9% methane), a laboratory for sample preparation and study, and freezers of "Grunland" type.

2.2   Experimental soil sample parameters and procedure of their preparation

Quartz sand of marine genesis was used as base soil. The sand was of light-gray color, with smoothed surface and homogeneously sorted. According to E. M. Sergeev's sand classification it is a fine-medium grained sand, see Table 1. Mineral composition, in accordance with the results of optical immerse analysis, is represented by quartz (more than 90%) and feldspat (10 %) and

Table 1. Particle size distribution of the soils used [%]

Particle diameter [mm]	1 ≀ 0.5	0.5 ≀ 0.25	0.25 ≀ 0.1	0.1 ≀ 0.05	0.05 ≀ 0.01	0.01 ≀ 0.005	0.005 ≀ 0.001	<0.001
Qartz sand	1	53	45	1	-	-	-	-
Montmorillonite clay	0.0	0.0	0.2	0.1	18.8	7.3	20.1	53.5

density 2.65 gcm^{-3}. The soil is characterized by low specific area - about 0.02 m^{2}g^{-1}.

Montmorillonite (bentonite) clay was of eluvial genesis. According to V. V. Okhotin's classification it was a heavy clay (Table 1). Montmorillonite prevails in clay fraction by more than 80%. The specific soil area is huge, about 620 m^{2}g^{-1}.

The clay content of the sand was 0, 2, 3, 5, 7 and 9% of the total sample mass. The initial water content (Wo) of the samples was the same in all experiments, 17%, and it was approximately equal to the optimum water content for most intensive hydrate accumulation (2/3 of the maximum water content). Distilled water was used.

In each experimental run two samples of the same composition and properties were prepared by the "layer-by-layer" compression method. One sample was for the experimental chamber, the second was the control sample; it was positioned near the chamber for temperature control and structure-change comparison.

2.3   Experimental procedure

The kinetics of the hydrate formation and the dissociation within the samples was documented when the temperature of the sample was varried in the hermetically closed pressurized chamber with hydrate-formation conditions. A sample was prepared (clay and water content, density control) and loaded to generate special conditions of the inner container of the chamber. Thereafter, the chamber was closed and blown through by methane to eliminate air. All this was done at room temperature. Then, the pressure inside the chamber was slowly increased up to $7-8$ MPa and the chamber was put into a freezer with temperature $+2 - +4°$C. Once the hydrate formation process was finished (registered by the pressure change), the temperature in the freezer was lowered down to $-6 - -7°$C and the sample was frozen and then recovered from the chamber.

When the cyclic hydrate formation was under study, the temperature within the freezer rose up back to room temperature, and then the hydrate

formation cycle was repeated without depressurization. Pressure changes during all experiments were regular and corresponded to the temperature change and the hydrate formation/decomposition.

When the chamber was opened at temperatures below 0°C (in the cold room), all samples were stable due to the self-preservation phenomenon (Ershov E.D. and Yakushev V.S., [3]); so there was a favorable possibility to study the structure changes of the samples during the hydrate formation. Recovered hydrate-containing samples were described, cut into 4 cylindrical pieces and water, gas, and hydrate content of each piece as well as density were determined.

3 Results of Experimental Study

3.1 Kinetics of hydrate formation and dissociation in the samples

The study of the pressure and temperature changes with time allows us to determine when and how much hydrates form within the sample. The total character of the pressure and temperature curves was the same in all experiments (Fig. 1). It is partly described by F. Wright et al. [8].
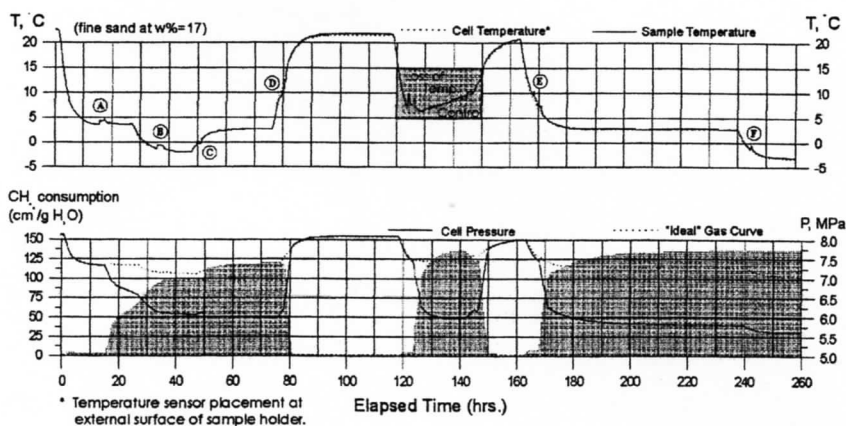

Fig. 1. Typical pressure/temperature record during experiments (according to F. Wright et al, [8])

Point A (Fig. 1) corresponds to the initial hydrate formation within the sample. Point B indicates sample freezing. Usually, the sample recovered subsequently, but in some cases, when cyclic hydrate formation was under study, a sample was heated and cooled again. In this case point C corresponded to secondary hydrate formation during ice melting within the sample. Point D

makes the final hydrate decomposition in the first cycle of hydrate formation/decomposition. Point E shows the initial hydrate formation during the second cycle and point F indicates the residual water freezing during the second cycle. Shadowed areas in the lower part of Fig. 1 reflect recalculated methane consumption into hydrate phase according to the pressure drop within the chamber.

The experiments have shown a considerable influence of freezing and cyclic repetition on equilibrium conditions and kinetics of hydrate formation within dispersed rocks. Equilibrium conditions of initial hydrate formation during the first cycle (A) were considerably different from the same conditions during the second cycle (E). Further repetition of hydrate formation produced no difference from the second cycle data. Secondary hydrate formation during the first cycle (point C) was unexpected and is explained by new possibilities for gas-water contact created by ice melting under hydrate-formation conditions.

The main methodical result obtained during the measurements of the kinetics was the correspondence between second-cycle-initial-hydrate-formation conditions and natural hydrate-formation conditions in sediments of the same properties and composition. So, probably, there is no longer any need to take into account supercooling needed for initiation of hydrate formation in nature. Equilibrium parameters of initial hydrate formation in natural sediments could be determined experimentally during the second cycle of hydrate formation. Equilibrium conditions of hydrate formation in dispersed rocks are different from the same conditions for pure water-free gas systems. They are shifted into thermodynamic conditions of higher pressures and lower temperatures, and this difference is growing with the rock-particle size and a decrease in the water content.

It is also worth mentioning that addition of clay particles to sand usually shifted equilibrium parameters of hydrate formation to higher pressures and lower temperatures, but sometimes a small pressure drop began at pressures lower than equilibrium for the system methane-pure water. This phenomenon still requires its explanation.

3.2   Structure and properties of hydrate-containing samples

In many samples recovered from the chamber hydrate caps of different thicknesses were observed at the top-exposed sides of the samples. In pure sand this cap was thickest and reached 12 mm. It was represented by white, relatively dense hydrate accumulation with inclusions of monolithic semi-transparent hydrate. This cap reflects strong water transfer in quartz sand during hydrate formation. However, addition of clay in proportion, (as small as 2% of the total weight) considerably decreased this cap formation and prevented water transfer along the soil samples. Thin caps (no more than 5mm thickness) were observed in samples with 2 and 3% of clay content, and in samples with 5, 7 and 9% of clay content this cap was practically absent.

At the same time, a clay-content increase resulted in more intensive hydrate-texture formation along the samples. In pure sand there is massive hydrate texture (hydrate-cement), in samples with 2 and 3% of clay some visible hydrate inclusions are formed. Further increase of clay content resulted in lens-like and porphyry-like (V. Yakushev [9]) hydrate-texture formation with thickness up to 1,5 mm and length up to 5-6mm.

Measurement of the final water content in samples showed considerable differences in the water distribution along samples in pure sands and those with clay (Figs 2, 3, 4, 5). In pure sand the water transfer was registered by drying of the central part (Fig. 2). Addition of montmorillonite clay reduced the water transfer very strongly, and with a clay content of more than 5% water transfer during hydrate formation was negligible.
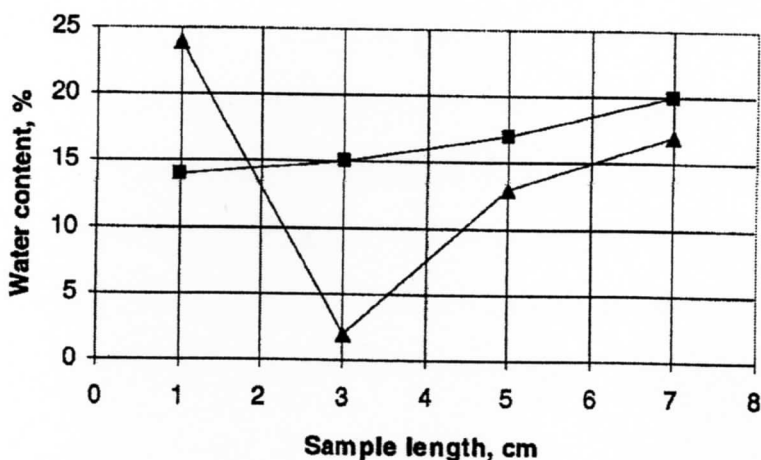

Fig. 2. Water content distribution along sand samples (Ac = 0%, Wo = 17%). ■ – control sample; ▲ – hydrate-containing sample

Gas (hydrate) content distribution within the samples was dependent on the water content and increased with the clay-content increase up to 7%. In pure sands, due to the low water content, the gas content is small and does not exceed 1 cm^3g^{-1} (Fig. 6). Addition of clay in small volumes (clay content (Ac) = 2%) does not change the gas content considerably. This is probably related to quick formation of an insulating hydrate film on water-gas contact within the sample and a reduction of the hydrate formation velocity. A further increase of the clay content results in more intensive hydrate accumulation, and the gas content is growing to approximately 5 cm^3g^{-1} at Ac = 7%. However, a further increase of the clay content decreases the gas content which could be attributed to decreasing the sample reservoir para-
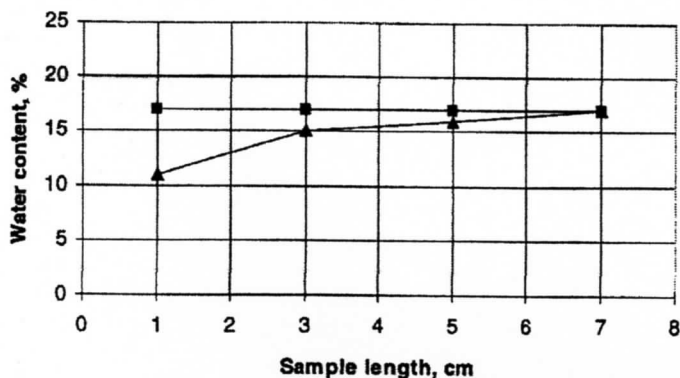
Fig. 3. Water content distribution along sand samples (Ac = 2%, Wo = 17%).
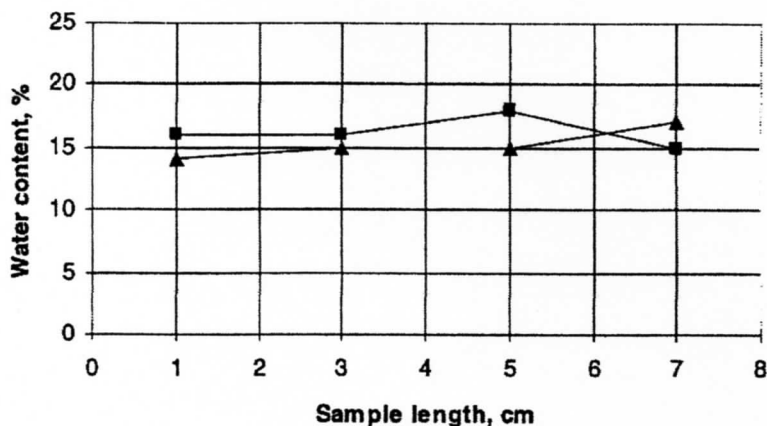■ – control sample; ▲ – hydrate-containing sample

Fig. 4. Water content distribution along sand samples (Ac = 7%, Wo = 17%).
■ – control sample; ▲ – hydrate-containing sample

meters which influence the growing bonded water content. So, probably for each permeable soil, there is an optimum value of the clay content at constant water content for maximum hydrate accumulation.

4   Conclusion

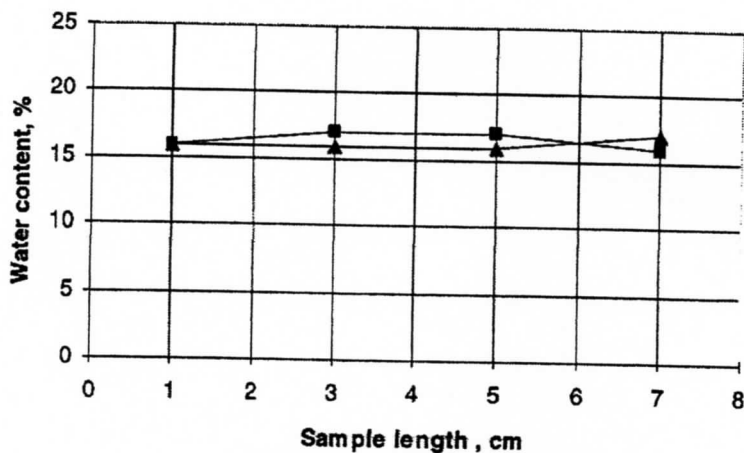The experiments conducted allow the following conclusions:

Fig. 5. Water content distribution along sand samples (Ac = 9%, Wo = 17%).
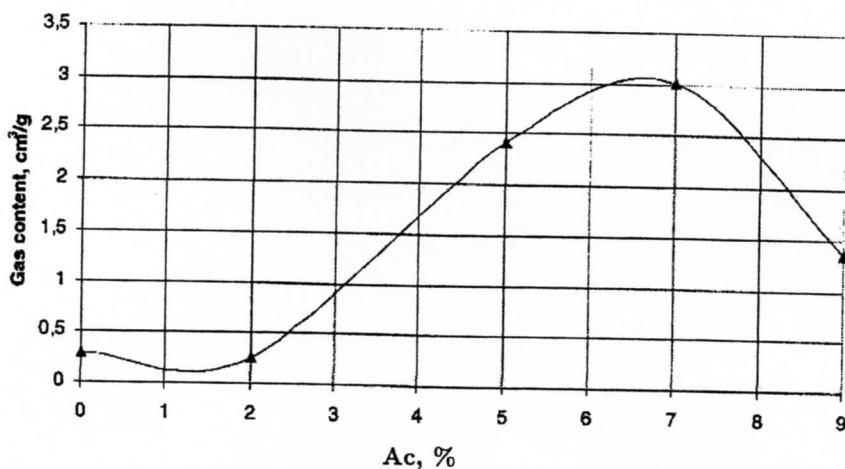■ – control sample; ▲ – hydrate-containing sample

Fig. 6. Experimentally determined average gas (hydrate) content of sand samples
of the same initial water content (Wo = 17%) with different clay content (Ac)

(1) Equilibrium conditions of hydrate formation in dispersed rocks are different from conditions for pure water-free gas system. The difference is growing with rock particle size and decreasing water content.

(2) Equilibrium conditions of hydrate formation in natural dispersed rocks can be determined experimentally during the second cycle of hydrate formation/decomposition; whereas the equilibrium conditions of hydrate

decomposition can be determined during the first cycle of hydrate formation/decomposition.

(3) If dispersed rock is frozen at hydrate-formation conditions, ice melting causes secondary hydrate formation, and hydrate content of the rock can grow considerably (Fig. 2).

(4) The second cycle of hydrate formation in dispersed rocks causes more intensive hydrate accumulation than first ones.

(5) Appearance of clay particles in sands strongly changes the character of hydrate accumulation decreasing water transfer during hydrate formation.

(6) The hydrate content of consolidated permeable sands is growing with the clay-content increase to an optimum value. Further increase of clay content considerably decreases the possibility for hydrate accumulation.

In addition the following result was found. Self-preservation phenomenon, when hydrates do not decompose completely at temperatures below $0°C$, after a pressure drop due to isolating ice-film formation on their surface, can be successfully applied when natural sample storage is needed and experimental studies of hydrate-containing rock structure are conducted. Recently published experimental results on superheated ice storage in hydrate envelope (L.Stern et.al. [6]) further the development of self-preservation phenomenon study; it can be applied to frozen rock storage and experimental studies at temperatures above $0°C$, if the ice within the rock is covered by hydrates existing at atmospheric pressure (for example, tetrahydrofuran hydrate). This is very important for the transport of the frozen samples from drill sites to the laboratory, when there is no possibility for constinuing cooling of the samples recovered.

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