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Laboratory studies of frozen natural and artificial hydrate-containing rock samples

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ABSTRACT

Different methods of laboratory and field study of hydrate-containing rocks were developed on a physical base of gas hydrate self-preservation phenomenon. Special experimental chamber was designed and constructed to study hydrate-formation and decomposition processes in laboratory conditions. Strong changes in the rock structure and mass-transfer during hydrate formation were observed in the course of experiments with dispersed rocks of natural composition as well as with specially processed samples of sands and clays. Permafrost cores containing gas hydrates were recovered during exploration drilling at Yamburg and Bovanenkovo gas condensate fields in West Siberia and investigated in laboratory conditions.

Further study of natural gas hydrate - containing deposits requires now experimental research in a very high degree. Exploration of hydrate-containing sediments especially inland needs very precise methods of well log as well as geophysical profiling. Technologies of gas recovery from hydrate-saturated deposits can be developed only on a base of experimental modelling. Field geologic studies are impossible without experimental modelling of hydrate accumulation and decomposition in different rocks and conditions. Although laboratory studies of pure hydrates have been well-known for a long time, laboratory studies of hydrate-saturated rock samples (especially saturated by methane hydrate) are much more limited. It is connected with much more complex technical and methodological problems which are needed to solve for successful experiment. One of the most difficult problems is impossibility of hydrocarbon gas hydrates exposition at atmospheric pressure that significantly narrows possibility of their experimental study.

It is necessary to mark that practically all known laboratory studies of hydrate-containing rock samples (1,2,3,4) were made mainly on specially prepared sand (or sandstone) samples saturated by tetrahydrofuran hydrates (which can not be encountered in nature) or by hydrocarbon hydrates, but without extraction from experimental chamber, so very restricted data have been received. Also there are not data concerning laboratory studies of hydrate-saturated rock samples at temperatures below 0°C. This study is needed for explanation of sudden gas blowouts from shallow permafrost section in the course of well drilling in polar regions (5).

METHODOLOGY

The laboratory studies of hydrate-containing dispersed rock samples have been started in VNIIGAZ and Moscow State University in the middle of 80-th and had initial purpose to investigate the tracks of methane gas hydrates after their decomposition in frozen soils caused by depressurization. Special experimental chamber

of high pressure was designed and constructed for hydrate formation in dispersed soils (6). Basic constructive difference from other experimental chambers applied by other researchers was in possibility of hydrate-containing sample extraction from the chamber after depressurization.

Methane hydrates had been planned to accumulate in porous space of wet dispersed samples (sands) and than to freeze them at hydrate-formation pressure inside the chamber. After pressure drop it was expected hydrate decomposition and partial destruction of the sample. But after first experiments there were not remarkable damages of the sample and very high specific gas content of the samples (up to $6 \text{ cm}^3/\text{g}$) when melted. So it was concluded that not all methane hydrates have decomposed in the samples and significant part of them can store in porous space at temperatures below 0°C and atmospheric pressure for a long time. These results allowed to apply for the obtained samples study usual laboratory methods developed for permafrost soils (7).

When the possibility of methane gas hydrates (cubic structure 1) and gas hydrates formed from mixture of methane and propane (cubic structure 2) existence in frozen soils at atmospheric pressure was proved in the course of experiments, it was logical to suppose existence of such "self-preserved" gas hydrates in upper part of permafrost above upper thermodynamic boundary of hydrate-stability zone. So different undisturbed permafrost cores from West Siberia were investigated in laboratory for gas hydrates dissipated in porous space by the methods developed earlier for experimental samples. Results indicated presence of self-preserved hydrates in some cores.

Experimental procedures for artificial dispersed rocks

In the course of the experiments quartz sands of various grain size, pure bentonite, distilled water and practically pure methane (99,99%) have been used. Sometimes thawed sediments of natural composition recovered from permafrost were under investigation too. Washed fine- and mid-grained quartz sands picked from the upper 100 m of the permafrost zone of Tazovskiy peninsula (North of West Siberia) and quartz-feldspar large-grained sands from the Moscow moraine were used (the grain gradation is given according to the classification of E.M.Sergeev (1973)). The sands were humidified by distilled water until their humidity reached approximately 0,5 of the capillary moisture capacity. During the experiment the sand was loaded into the cylindrical container, 10 cm in length and 4 cm in diameter made from chromium-plated copper. The inner walls of container were covered by a layer of plastic heavy clay in order to prevent gas flow along the walls. The bottom of the container possessed a hole, 0,5 cm in diameter, for gas supply into a sample.

The container was put into experimental pressure chamber into which methane flowed. The chamber was closed hermetically and after short period of methane blowing through the sample, the gas pressure was increased up to 10 MPa at a temperature $+20^\circ\text{C}$. After that the chamber was separated from the gas cylinder and was placed into the air freezer with temperatures about $+2 - +4^\circ\text{C}$.

The hydrate formation process had been registered by pressure and temperature changes in the chamber (fig.1). The pressure decreased until all free water in the cell was transformed into hydrate. After pressure stabilisation the temperature in the freezer lowered down to $-5 - -15^\circ\text{C}$. When the temperature in the chamber and in the freezer came into equilibrium, the pressure in the chamber during 1-3 minutes

had been lowered to atmospheric value. The chamber was opened, the sample extracted from the container by special piston and then the sample investigated for hydrate content and some other properties.

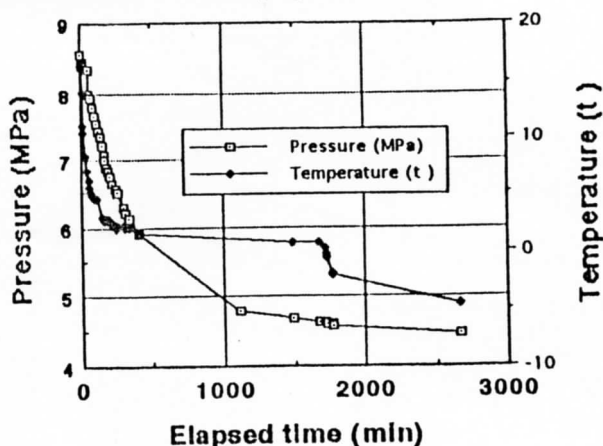


Figure 1. Pressure-temperature changes in the course of methane hydrate formation in fine-grained quartz sand of natural composition recovered at Bovanenkovo field (Initial humidity 26,9%).

Hydrate saturation of clays is a more complex task. To investigate possibility of hydrate formation in bentonite special experiment was made. Bentonite sample was dried at 105°C for a day. Dry clay was pounded into fine powder, cooled down to -10°C and mixed with fine snow in the proportion providing the clay humidity lower than maximum hygroscopic moisture value (for bentonite about 15%). The mixture was put quickly into the container at temperature -7°C and closed in the experimental chamber. Methane pressure in the chamber was risen up to 7 MPa at temperature -7°C.

The main purpose of the experiment was observation of bounded water influence on hydrate formation process. In the course of experiment dry bentonite powder took the water from snow for bounded water layer formation, from the other side hydrate formation transformed remaining part of snow to gas hydrate. These opposite processes are reflected at the pressure curve (fig.2). At the first stage (AB) pressure drop caused by hydrate formation from snow took place. After all snow transformation into bounded water or gas hydrate, hydrate decomposition has began and pressure had grown until all hydrates decomposed (BC). Testing of the sample for gas hydrate presence after extraction from the chamber gave negative result.

Other bentonite powder sample was mixed with snow in proportion providing humidity of upper plastic limit (about 65%). Hydrate formation registered by pressure drop in the chamber took place for a long time (more than 1 day) and required additional volumes of methane. After the sample extraction from the chamber its gas content when melting was about 36 cm³/g.

Experimental procedures on main properties definition for artificial and natural hydrate-containing rock samples.

After extraction of the samples from the chamber, each was cut in 5 equal parts of 2 cm width. The density, humidity, gas content were determined for every part. The same procedure was made for natural permafrost sand samples recovered at

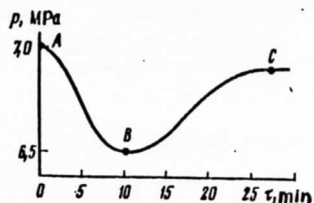


Figure 2. Pressure change at hydrate-formation conditions in experimental chamber with bentonite sample of low humidity (about 12%).

Tazovskiy peninsula (Yamburg gas-condensate field) and Yamal peninsula (Bovanenkovo gas condensate field, West Siberia). For artificial samples these properties were compared with the same ones before hydrate formation. Gas content was recalculated to methane hydrate content (with chemical formula $M \cdot 6,0 H_2O$) and compared with possible free gas content in porous space. Those samples where liberated gas volume when melting exceeded free porous volume more than 2 times were attributed to hydrate-containing.

Structure of the samples was investigated by microscopic observations. Sometimes for the samples with relatively small hydrate content plexy glass replicas were used (plexy glass solution in dichlorethane). For some samples one-axis flash compression resistance was determined to compare hydrate-containing samples mechanical properties with the same of frozen samples.

SOME RESULTS

Humidity.

Humidity determination was made before and after hydrate formation in artificial samples. Every time when hydrate formation took place in sands strong mass-transfer was observed. After samples extraction from the chamber open surfaces of the samples were covered by white caps of methane hydrate. Study of humidity distribution along the samples showed accumulation of water in hydrate state at the edges of samples and drainage of the central parts (fig.3). It is necessary to mark, that such strong mass-transfer was not registered in the same experimental conditions when clays were under investigation.

Density

Density of the artificial sandy samples had changed not very remarkable. In central parts of the samples there was increasing of density up to 10 % in comparison with edge parts, depending on initial water content and intensity of mass-transfer.

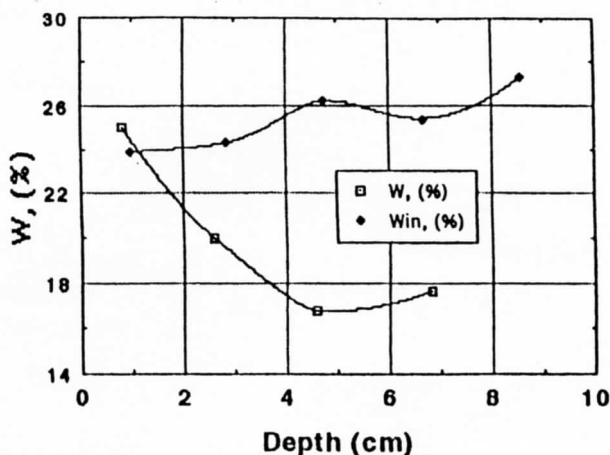


Figure 3. Water content distribution in Bovanenkovo fine-grained sand before hydrate-formation (W_{in}) and after hydrate-formation (W).

Gas and gas hydrate content.

Gas content in artificial hydrate-containing samples corresponded to hydrate content and humidity of different parts of a sample. Most values of gas content (up to 10 cm³/g) were registered when hydrates have been formed in fine-grained sands with high initial humidity (fig.4). Possible hydrate content increases with dispersity degree of sands. It is low in large-grained sands and high in fine-grained. Appearance of clay particles in porous space of sands decreases possible maximum hydrate content although leads to increasing of humidity.

Hydrate content definition in natural permafrost cores showed low content of hydrates in permafrost above upper part of hydrate-stability zone (table 1), but it is necessary to mark that it is practically first experience of such study and cores were taken casually without special preliminary exploration of the recovery areas.

Inner structure description

Microscopic investigations of artificial hydrate-saturated samples allowed to prove that hydrates accumulates in porous space as films on mineral particles surfaces, groups of small thin crystals, especially along contacts of mineral particles. More large hydrate inclusions (hydrate textures) were made from thin crystals accumulations or sometimes from monolithic semi-transparent hydrate.

Hydrate textures had formed at places of the sample heterogeneities (inclusions of clay or organic materials in non-washed sands, places of local density decreasing et al.). Following types of hydrate textures were registered: massive, crust-like,

porphyry-like, lens-like and layered. Hydrate textures (schlirrens) were composed by accumulations of small needle-like crystals resembling the solid snow. Often hydrate inclusions in the pore space had a porous structure which permits the free filtration of the gas. Apparently, inclusions of such structure decompose first when

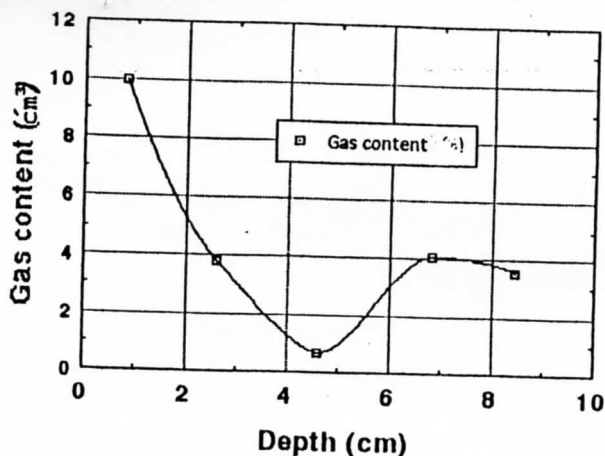


Figure 4. Gas content distribution along sample of Bovanenkovo fine-grained sand when hydrates decompose.

pressure drop takes place. However pores completely filled by the white hydrate which had no visible porosity were observed too.

Table 1. Hydrate content definition in permafrost samples from Yamburg and Bovanenkovo gas condensate fields (West Siberia).

Lithology	Depth, m	Density g/cm ³	Humidity, g/g	Porosity, cm ³ /cm ³	Free porous volume, cm ³ /g	Specific gas content, cm ³ /g	Hydrate content, g/g
Yamburg Shale	71	1,87	0,20	0.42	0,01	0.22	0,0012
Yamburg Fine Sand	110	2,01	0,16	0,36	0,01	0,20	0,0010
Yamburg Shale	118	1,86	0,18	0,41	0,04	0,21	0,0009
Bovanen. Shale	86	1,81	0,275	0,50	0,002	0,02	0,00001

Mechanical properties

Estimation of mechanical stress capacity was made for fine-grained sand with initial humidity 15% and at temperature -6°C. Two samples were prepared: one methane hydrate-saturated and one frozen at the same temperature without hydrates. All other properties and sizes of the samples were equal. One-axis compression was applied for stress capacity determination. This parameter was equal to 0,49 MPa for hydrate-saturated sample and 0,05 MPa for frozen one. So hydrate cementing process make sediment more firm than freezing. Apparently humidity and temperature influence on mechanical properties should be more remarkable in hydrate-saturated deposits.

Study of gas hydrate decomposition kinetics in sandy sediments

This study was executed for the GAZPROM to determine the risk for drilling in north regions and offshore where hydrate-saturated deposits can be encountered. Measurement of pressure-temperature dynamics during hydrate decomposition in sands of different humidity, grainity and mineralogy showed strong influence of these parameters on the decomposition kinetics. The more is humidity (and hydrate-content) the lower is decomposition velocity, the more gas volume should be liberated. And vice versa: the more is sand particles size, the less is humidity (hydrate content) and the more is decomposition velocity. So most risk for drilling should be in large-grained sands, where hydrates are decomposing most quickly.

CONCLUSION

Executed studies allow to make following main conclusions:

1. The gas hydrate self-preservation phenomenon allows gas hydrates to exist in nature from first meters of permafrost zone and it strongly expands area of gas hydrates existence in cosmic space.
2. Very remarkable mass-transfer takes place in porous deposits in the course of hydrate-saturation process.
3. Hydrate accumulation in dispersed sediments strongly changes inner structure of the rock.
4. Kinetics of gas hydrate decomposition in porous space depends on deposit grainity, humidity, mineralogy and porosity.

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