Experimental investigation of the possibility of relict gas hydrates formation in frozen sediments

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***Abstract*. Permafrost section has an ability to accumulate natural gas. The presence of great accumulations of natural gas in the mass of frozen sediments is fixed at drilling of various wells in the Arctic areas. Thus gassing from the section of frozen sediments reaches hundreds and thousands of cubic meters a day. The accumulations of natural gas at shallow depth in the mass of frozen sediments are great hence there is a big interest in their practical use and in an estimation of their ecological influence on the environment.**

The special analysis of gas releases from shallow horizons of frozen sediments allows speaking that a part of these gas shows is connected with relict gas hydrate formations which could be kept in the permafrost section owing to the self-preservation effect of gas hydrates. For a substantiation of this statement the complex of experimental investigations was lead. These researches involved an artificial accumulation of methane hydrate in freezing sediments, including sediment samples recovered from gas showing permafrost horizons, and studying of the effect of self-preservation of gas hydrates in frozen soil samples at decrease of equilibrium pressure. During the conducted experiments the factors and conditions which promote development of effect of self-preservation have been revealed. Thus the opportunity of existence of relict gas hydrate formations in the north of West Siberia is shown by the example of samples taken from gas showing horizons.

***Index Terms*— methane, shallow permafrost, relict gas hydrates, self-preservation effect.**

I. Introduction

Permafrost sediments occupy significant part of the Arctic areas of continental Eurasia, America. Their thickness reaches 300-700 meters [1]. Geological studying and temperature modeling of underwater conditions show that permafrost can also exist within the limits of a continental shelf of the Arctic seas. Frozen sediments on a shelf can meet up to 60 meters isobath. As the Arctic seas are shallow, the shelf frozen ground can occupy greater territories, thus its thickness can reach 200-300 meters [2]. Processes of cooling and long-term frost penetration which periodically occurred in Arctic regions promoted formation of not only powerful thicknesses of frozen sediments, but also gas hydrates congestions, first of all methane gas hydrates. Gas hydrates represent ice-like crystal connections which are formed of water and natural gases, such as methane, CO_2 etc, in conditions of lowered temperatures and increased pressure. Since each volume of methane hydrate can contain as much as 184 volumes of gas, hydrates are currently considered a potential unconventional energy resource [3]

The zone of stability of gas hydrates formations in cryolitozone where methane gas hydrates can be formed and exist, begins with depths of 200-250 meters and extends in sub-permafrost layers up to depths of 800-1500 meters. A stock of gas in hydrate form on land by different estimations ranges from $3,1*10^{13}$ up to $3,4*10^{16}$ m^3 [4]. Stocks of methane in hydrate form within limits of a continental shelf of the Arctic seas is difficult to estimate as these areas remain little-investigated.

Recently there were data which allow to speak about an opportunity of methane gas hydrates existence in thicknesses of frozen sediments above zone of stability (up to depths of 200-250 meters), in so-called zone of metastability of gas hydrates [5], [6]. These "relict" gas hydrate formations in permafrost could be formed earlier when there were favorable thermo-pressure conditions. Later as a result of regress of sea or glacier recession they have appeared in the metastable (inhibited) condition owing to display of self-preservation effect [7]. Presence of relict gas hydrate formations in permafrost of Arctic regions can essentially raise its power resources. As relict gas hydrate formations occur at small depth and are in metastable condition their development and exploitation can be easier realized.

On the other hand, relict gas hydrates on small depth in cryolitozone, can represent essential geological danger at natural and technogenic degradation of frozen ground as at their decomposition a plenty of methane which possesses very strong hothouse properties can be thrown out in the atmosphere. Besides that various technical complications caused by emissions of gas and ground down to occurrence of fires are possible at

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drilling and operation of various trade wells in areas of relict gas hydrate formations distribution.

That's way special consideration of metastable gas hydrate formations in frozen sediments is necessary.

II. Gas and Gas Hydrates in the Shallow Permafrost

Gas evolutions from shallow permafrost connected with relict gas hydrates have been fixed in many Arctic areas of Russia, Canada (fig.1). So, in delta of Mackenzie river three samples of frozen hydrate-comprising core have been taken at drilling of a well in area of gas field TAGLU. Two of them had clay structure and contained visible inclusions of gas hydrates, and significant volume of gas essentially surpassing the volume of pore space was allocated from the sandy sample at thawing. The sandy sample has been taken from an interval above a modern roof of zone of stability of hydrates, and presence of hydrates in it can be explained by effect of self-preservation of gas hydrates at negative temperatures [8]

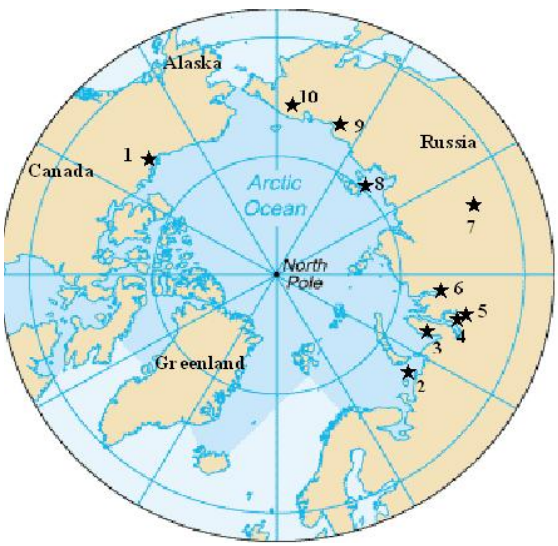

Fig.1. Location of fixed gas and hydrate displays from shallow permafrost in Arctic regions.

1-Taglu gas field; 2-Shelf of Pechora Sea, 3-Bovanenkovo gas field; 4-Yamburg gas field; 5-Zapolyarnoe gas field, 6-Pelatkino gas field; 7-Yakutian diamond fields; 8-Shelf of Laptev Sea 9 Kolyma gold bearing placers; 10-Chukotka gold-bearing placers

In Russia intensive gas evolutions from zone of metastability of gas hydrates were observed in permafrost in the European North, in Siberia, on Chukotka [6], [9]. Besides that gas shows possibly connected with gas hydrates have been fixed on continental shelf of the Arctic seas. In particular powerful emission of gas (methane) from a well drilled in frozen sediments on a shelf of the Pechora sea [10] is noted. Gas-yielding layers belonging to shelf frozen ground are found out in the Laptevs' sea [9]. On a number of indirect attributes given gas evolutions are connected with decomposition of pore gas hydrates which are in metastable (inhibited) condition.

III. Gas Shows in the North of West Siberia

Numerous gas shows from zone of metastability are fixed in the north of Western Siberia within the limits of Yamals (Bovanenkovo gas field), Tazovskiy (Yamburg gas field) peninsulas. One of the first areas where attempt of studying of intrapermafrost gas congestions has been undertaken is area of Yamburg gas field. During drilling gas comprising samples have been lifted from depth of 70-120 m. Gas in gassy intervals of frozen sediments consisted mainly of methane (91,5 %) and had biochemical origin. Raised pressure of gas, smell of hydrogen sulphide which could be kept in cryolitozone only in hydrate form, strengthening of gas shows intensity at thawing of borehole environment and their attenuation at the termination of thawing, and also high gas comprising of frozen core at low free porosity testify about possible gas hydrate finding of part of intrapermafrost gas [11].

On Yamal peninsula within the limits of southern part of Bovanenkovo gas field detailed studying of gas congestions in permafrost [5] also has been lead. On the basis of data analysis received from 40 wells, drilled by scientific and technical firm Krios on full thickness of permafrost it has been established, that gas evolutions from permafrost intervals are fixed on depths from 20 up to 130 m, and debits of gas reach 10-14 thousand m^3/day. In chemical compound of the gas selected from permafrost intervals methane having biochemical origin prevails. Some laws connecting gas comprising of frozen sediments of area of researches with their structure, compound and properties have been revealed. So all gas evolutions are dated for horizons and prolayers of peated sand, meeting in cut of permafrost sediments up to depths of 130 m. Besides that increasing in general salinization of sediments below horizons of fixed gas shows is connected with gas emissions to soil zones with lowered salinization that can testify about cryohydrate release of salts. Decrease in the general salinization of sediments in gas showing intervals in most cases coincides with local minima of the maintenance of not decayed fossils. The led analysis of thermal physical characteristics of soil thickness has revealed the certain tendency of reduction of frozen grounds heat conductivity in gas showing samples in comparison with samples of not gas showing horizons. Special laboratory researches of gas comprising samples of frozen sediments selected from gas showing horizons have shown that the quantity of gas in them exceeds free porosity on 2 - 3 orders. The received laws testify about opportunities of finding of part of gas in the form of relict gas hydrate formations which were preserved in top horizons of frozen ground due to display of self-preservation effect.

IV. Experimental study of self-preservation effect of gas hydrates in frosen sediments

For acknowledgement of self-preservation gas hydrate formations opportunity in permafrost sediments complex of special experimental researches has been led. It included artificial accumulation of methane hydrate in freezing sediments, and studying of gas hydrates self-preservation effect in frozen soil samples at decrease of equilibrium pressure. As object of research samples of the core selected from gas showing horizons of permafrost on Yamburg gas field (dusted sand, depth 63 meters), and also on Bovanenkovo gas field (easy loam, depth 65 m) have been used. In sand the fraction of 0,25-0,1 mm (47,3 %) prevailed, the maintenance of dusted fractions (size of particles 0,05-0,001 mm) made 14 %, and the maintenance of clay fraction (size of particles less 0,001 mm) about 2 %. In mineral structure quartz - 80 % - prevails. Salinity of ground made about 0,09 %. The sample of loam was characterized by prevalence of fraction of 0,1-0,05 mm (43,8 %), the maintenance of dusted fractions made 25,5 %, and the maintenance of clay fraction -11 %. In the general mineral structure quartz, albite and microwedge prevail. In clay fraction illite and peach prevail. Salinity of ground made 0,69 %. In experiments the following values of initial humidity were set: for dusted sand 14 %, 18 % and 20 %, for easy loam about 20 %.

The technique of experimental researches has been based on physical modeling of phase transitions of moisture in methane-saturated grounds in pressure chamber and subsequent research of artificially hydrate-saturated samples in frozen condition [12]. Making of artificially hydrate-saturated environments was carried out in two pressure chambers in which containers with a damp ground were located. In the first pressure chamber the size of sample of a ground made 4,6 cm in diameter and about 9 cm in length, in the second pressure chamber of 6,8 and 9 cm accordingly. Methane (99,98 %) was used as hydrate-gen gas.

Hydrate-saturation of ground samples in a pressure chamber was carried out at low positive temperature (~0,5-2,0 ^{o}C). After the termination of hydrate accumulation process in ground, the pressure chamber with the soil sample was cooled up to -8 ^{o}C. Thus residual pore moisture which has not passed in hydrate froze. As a result frozen hydrate comprising samples which were in equilibrium conditions turned out. Their hydrate comprising and hydrate coefficient (share of moisture which has passed in hydrate) were supervised according to change of thermobaric conditions during experiment. For this purpose calculation under gas laws in view of compressibility of gas was spent.

Further pressure in a chamber with frozen hydrate comprising sample was released up to atmospheric pressure, then the pressure chamber opened in a refrigerating room at temperature -8 ^{o}C.

After opening of pressure chamber frozen hydrate sample was taken from a chamber and was exposed to detailed petrophysical researches. As a rule it occurred in 30 minutes after pressure release. Petrophysical researches included macro-and micromorphological supervision, level-by-level definition and calculation of humidity, density, gas and hydrate comprising, porosity, hydrate coefficient, degrees of hydrates and ice pore filling. Definition of samples gas comprising was carried out by measurement of gas volume allocated at thawing tests in sated solution of NaCl. Calculation of methane hydrate maintenance was spent according to gas comprising, using hydrate number 5,9.

Then remained frozen hydrate comprising ground was located in weighing bottles for long storage at negative temperatures. For prevention of sublimation samples were fallen asleep by an ice crumb. Later in certain intervals of time tests for the control over change in time of gas and hydrate comprising from stored at negative temperatures hydrate comprising samples were selected. Definitions proceeded before attenuation of pore hydrate decomposition process or the full charge of hydrate comprising ground. Duration of supervision reached one month and more. On the received data schedules of change in time of gas evolution intensity (Q_g), hydrate comprising (H_v), degrees of hydrates (G_h) and ice (G_i) pore filling, hydrate coefficient (K_h) were under construction.

V. Results of experimental researches

During the executed experiments on artificial methane gas hydrate accumulation in pore space of soil samples and their subsequent cooling up to negative (-8 ^{o}C) temperatures hydrate comprising frozen samples have been received.

In general they were characterized by rather homogeneous structure and uniform distribution of hydrate and ice in pore space of samples on their height. It was supervised by creation of favorable conditions for hydrating in an initial state of samples (uniform distribution of humidity and developed gas-water contact in pore space) that proved to be true results by level-by-level definition of the basic water physical characteristics of samples. It enabled calculation of average values of petrophysical parameters for the whole frozen hydrate-saturated sample in conditions of balance (in a pressure chamber) and in nonequilibrium conditions (in 30 minutes after pressure release to atmospheric).

The received samples were characterized by massive cryohydrate structure. Porosity of artificially hydrate-saturated samples of grounds changes in an interval 0,41-0,44, thus the density for sand made 1,63-1,76 g/cm^3, and for loam - 1,82 g/cm^3. The share of moisture passed in hydrate (K_H) in sand (in equilibrium condition before pressure release) reached 0,76, and saturation of pore space by hydrates-0,6. In 30 minutes after pressure release (K_H) did not exceed 0,68 and hydrate-saturation 0,45. For more disperse sample of easy loam values of (K_H) and hydrate-saturation made accordingly 0,12 and 0,11. And after pressure release accordingly 0,11 and 0,10.

Experimental studying of methane gas hydrate dissociation in frozen samples after pressure release shows that in the first moment after pressure release there is rather intensive decomposition of pore hydrate, then intensity of decomposition falls, and later practically fades (fig. 2).

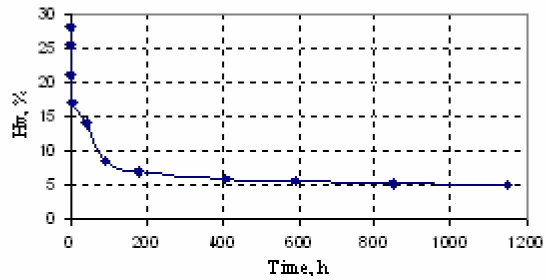

Fig. 2. Methane hydrate dissociation kinetics in artificially hydrate-saturated frozen sample of sand (W=18 %, t = -6,5 ^oC) after pressure release to 0,1 MPa.

First 100 hours of supervision decomposition of almost 2/3 pore hydrates occur, however then dissociation process gradually fades, and in 800 hours practically completely stops, thus residual hydrate comprising makes about 5 %. Thus, incomplete decomposition of pore hydrate, caused by self-preservation display effect is observed. The self-preservation effect consists in formation of ice pellicle around particles of decaying gas hydrate which is formed of the water phase arising at superficial decomposition of gas hydrate in conditions of negative temperatures. As a result of this effect the remained part of not decayed pore hydrate can be in metastable condition for a long time [7].

Hydrate-saturation falls at decomposition of hydrate in pore space. This process, in its turn, makes active the process of transformation of the formed water in ice. Thus simultaneously with falling of hydrate-saturation the degree of pore filling with ice (G_i) (fig. 3) increases. So if in the beginning of experience the degree of pore filling with hydrate made 46 %, and saturation of pores with ice - 3 %, in 845 hours G_H has decreased to 10 %, thus saturation of pores with ice made 43 %.

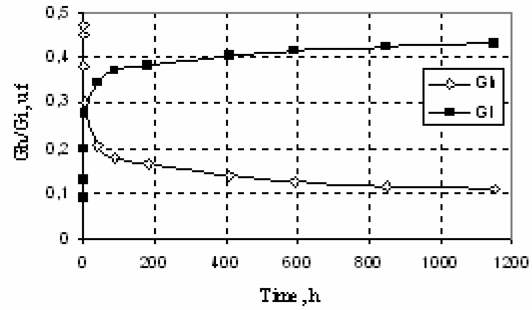

Fig. 3. Change in time of degree of pore space filling with methane hydrate (G_h) and ice (G_i) in the sample of hydrate-saturated sand (W=18, t = -6,5 ^oC) after pressure release to 0,1 MPa.

Thus, ice formed at dissociation promotes attenuation of gas hydrates decomposition and increasing of gas hydrate formations stability in frozen sediments.

The experiments show that self-preservation gas hydrate formations in frozen sediments depends on many factors such as thermobaric conditions, ice content, phase structure, gas permeability, structure of organ-mineral skeleton of sediment, salinity, structurally-textural features of hydrate comprising sediments, including micromorphology of gas hydrate formations.

Ice which is formed at frost-killing of residual pore water which does not transformed into hydrate plays the special role in self-preservation of gas hydrates. Occurrence of this ice promotes increasing of gas hydrate formations stability in pore space and their primary preservation. As a rule samples of frozen hydrate comprising sediments with greater ice content after pressure release below equilibrium differ by faster attenuation hydrate dissociation. Increasing of dispersiveness and maintenance of clay particles reduces hydrate coefficient and raises hydrate dissociation intensity. However in more disperse loamy adjournment self-preservation of pore gas hydrates is observed. So in the sample of frozen artificially hydrate-saturated loam residual volumetric hydrate comprising of gas hydrate after attenuation of dissociation made several percent.

Results of experiments executed on sand and loam samples show that intensity of pore gas hydrate formations dissociation sharply decreases in time with downturn of temperature. So in the sample of sand (W=14 %, Yamburg gas field) at high negative temperature -2 ^oC hydrate-saturation after pressure release has fallen up to 0,05 in 20 hours, at -4 ^oC made 0,28, and at -7 ^oC has decreased only up to 0,43. (fig. 4).

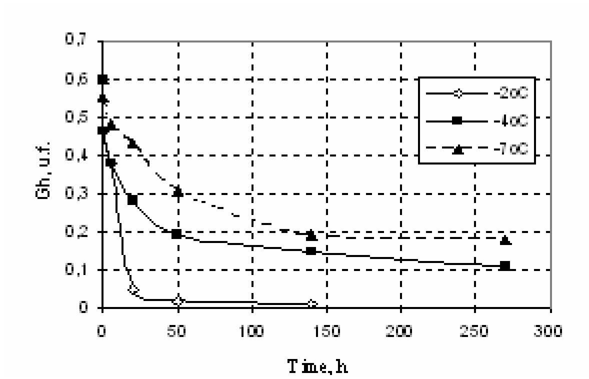

Fig. 4. Methane hydrate dissociation kinetics in artificially hydrate-saturated frozen sand (W=14 %) after pressure release to 0,1 MPa.

In 150 hours at temperature -2 °C hydrate has practically decayed, and at temperature -4 °C and -7 °C was kept, and process of its decomposition has sharply decreased, especially at temperature -7 °C.

At increase of initial humidity in the sample of sand up to 18 % methane hydrate dissociation intensity is noticeably slowed down (fig. 5).

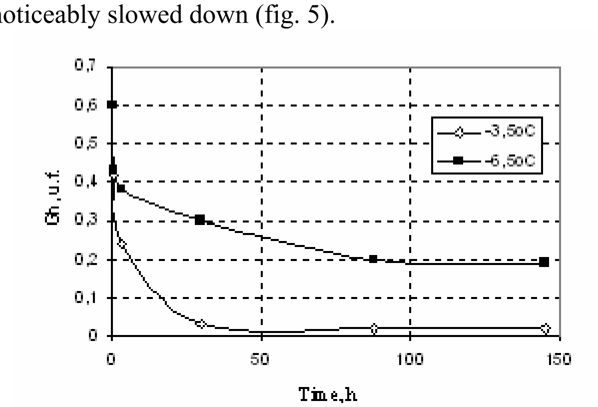

Fig. 5. Methane hydrate dissociation kinetics in hydrate-saturated frozen sand (W=18 %) after pressure release to 0,1 MPa.

At temperature -7 °C process of pore hydrate decomposition has practically stopped in 90 hours after pressure release. At more heat (-3,5 °C) the degree of pore filling with hydrate also did not vary in time, however its value made only 0,02.

In hydrate-saturated frozen sample of loam supervision over pore hydrate dissociation process at pressure release were spent at three various temperatures: -3, -5,5 and -13 °C. Delay of hydrate dissociation process was observed for all temperatures, however attenuations of pore hydrate dissociation process was fixed only at -5,5 °C and -13 °C, and residual hydrate-saturation was at temperature -13 °C higher and made 0,07on the end of experiment.

Thus the received experimental data testify that practically full attenuation of pore hydrate dissociation process occur with downturn of ambient temperature. Comparing these temperatures with temperature conditions of ground beddings in nature (-5 °C, -7 °C for permafrost sediments of Yamburg and Bovanenkovo gas field), it is possible to speak about an opportunity of gas hydrate formations in a metastable condition existence within the limits of the given areas.

It is necessary to note that in-place conditions the baric factor which is created by weight of overlying soil thickness and also high ice content of adjournment will give additional stability to hydrate comprising adjournment which are in nonequilibrium conditions.

VIII. Conclusions

The analysis of field materials on research of top horizons gas comprising of frozen thicknesses allows to speak about an opportunity of relict gas hydrate formations existence on small depth (20-200 m) above zone of stability of gas hydrates, that can be connected with geological display of self-preservation effect of gas hydrates in frozen sediments. Direct and indirect attributes of gas hydrates presence in cryogenic sediments prove it.

Special experimental researches on artificial accumulation of gas hydrates in the freezing sediments executed on core samples of sediments selected from gas showing horizons within the limits of Yamburg and Bovanenkovo gas fields confirm an opportunity of long preservation of pore gas hydrate formations in frozen sediments at bedded negative temperatures and pressures below equilibrium owing to self-preservation effect. Favorable factors promoting geological displays of self-preservation effect of gas hydrates are low temperatures, high ice content, low gas permeability, and also raised (higher than atmospheric) pressure upon gas shows depths that will promote existence of metastable (relict) gas hydrate formations in frozen sediments

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