SPE SPE-166925

Relic Gas Hydrate and Possibility of their Existence in Permafrost within the South-Tambey Gas Field

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Abstract
Isolated gas and gas hydrates in the permafrost are serious geological danger in the process of oil and gas field development in Arctic. The particular hazard is the largegas accumulations confined to the sand and loamy sand horizons in the permafrost at depths down to 200 meters. Such gas accumulations are found in a number of Yamal gas fields and South-Tambey gas field among them. There are some indirect signs that they may be relic gas hydrates formed earlier in specific hydrate accumulation conditions. Up now they might have been preserved in the permafrost due to the effect of gas hydrate self-preservation at temperatures below zero. These gas hydrates lying above the modern gas hydrate stability zone are in a metastable state and very sensitive to various anthropogenic influences. While drilling and during borehole operation of in the areas of relic gas hydrates locations various technical complications up to bow out may occur.

To evaluate the possibility of formation and existence of relic gas hydrates on the territory of the South-Tambey gas field the mathematical simulation and experimental modeling were performed. The aim of mathematical simulation was to understand the dynamic of the permafrost thickness and of the zone of gas hydrates stability (GHSZ) in the Late Pleistocene and Holocene. The simulation allow to present the evolution of the permafrost during which the zone of gas hydrates stability started from the earth's surface being located within permafrost. As the permafrost has never fully thawed, near surface horizons may still contain relic gas hydrates to this day.

Experimental researches were undertaken to study the possibilities of preservation of relic gas hydrates in the permafrost of the South-Tambey gas field up to now. The experiments consisted of two stages. The first part was the artificial saturation of field samples by methane hydrate. At the second stage we studied processes of self-preservation of pore gas hydrate in the frozen samples under nonequilibrium conditions close to the reservoir conditions such as temperatures -5...-6 0C and pressure of 0,6-1,3 MPa. These experiments highlignt the high stability of the pore gas hydrates in the frozen samples at the given nonequilibrium conditions.

In general we can make a conclusion that the existence of relic gas hydrates on the territory of the South-Tambey gas field at depths of less than 200 m in the permafrost is possible.

Introduction
Isolated gas and gas hydrates are serious geohazards in the process of oil and gas field development (Are, 1998; Yakushev & Chuvilin, 2000; Dallimore *et al.*, 2001). The particular hazard is the large gas accumulations confined in the sand and loamy sand horizons in the permafrost at depths up to 200 meters. Such gas accumulations are found in a number of Yamal gas fields and South-Tambey gas field (STGF) among them.

There are some indirect signs that they may be relic gas hydrates formed earlier in specific hydrate accumulation conditions (Chuvilin *et al.*, 1998; Yakishev, 2009). Up to now, they might be preserved in the permafrost due to the effect of gas hydrate self-preservation at temperatures below zero. These gas hydrates lying above the modern gas hydrate stability zone are in a metastable state and very sensitive to various anthropogenic influences. While drilling and during geotechnical operations in the areas of relic gas hydrates locations, various technical complications up to blow out may occur.

The reasons of occurrence of gas hydrates in permafrost at shallow depths

It is known, that the stability zone of natural gas hydrates is in the range of 250-300 meters deep in permafrost areas (Istomin & Yakushev, 1992; Collett & Dallimore, 2000). It can rise up to 200-150 meters deep with an increased content of more severe homologues of methane (ethane, propane, etc). However, in the process of epigenetic freezing of deposits, necessary conditions to hydrates' formation can occur at lower depths due to crystallization of pore water in confined volumes and cryogenic gas concentration in the sand lenses and horizons. Another possible reason of gas hydrates' formation at shallower depths in permafrost is pressure factor caused by glaciation or transgression of the Arctic seas (Romanovsky,1993; Trofimuk *et al.*, 1986; Romanovsky & Hubberten, 2006). As a result, intrapermafrost gas accumulations at lower depths could be within the gas hydrate self-preservation zone and transformed into gas hydrate (Chuvilin *et al.*, 1998; Yakushev, 2009; Chuvilin, Lupachik, 2011). Following regressions of the seas or glaciers retreats, gas hydrates may be preserved above the theoretical GHSZ. Such preservation could be due to the self-preservation process and transform into relic condition in the absence of heating from surface.

In this work, the possibility of formation and existence of relic gas hydrates in upper horizons of permafrost is considered in areas of South-Tambey gas field. These researches are based on mathematical and experimental modeling carried out for the study area.

Mathematical modeling of permafrost thickness and gas hydrate zone stability

The aim of mathematical modeling is the clarification of the possible existence of the gas hydrate stability zone at shallow depths; they may have been preserved in a metastable state to this day. For this purpose, we use a retrospective approach, which was elaborated and tested in the context of the East Siberian arctic shelf (Romanovsky & Tumskoy, 2011).

The mathematical model used in this study is based on the enthalpic description of phase transitions suggested by Samarskii and Moiseenko (1965). The temperature field $t(x, y, \tau)$ is computed as the general solution to the quasilinear equation of heat conductivity that expresses the law of energy conservation with due account for the energy of phase transitions. In our model, it is assumed that the decomposition of hydrates takes place within thousands of years and that the system is open and characterized by the steady-state pressure equal to the hydrostatic pressure. Thus, it is assumed that the rate of changes in the pressure field (pressure deviations from the hydrostatic pressure) is much higher than the rate of changes in the temperature field upon the formation of gas hydrates. Under this assumption, equilibrium curve for hydrates is a function of the depth. The upper boundary of the calculated rectangular area corresponds to the earth surface accounting for the paleoclimatic curve and the curve of sea level changes. At the side boundaries the homogeneity of the Neumann boundary conditions is considered (i.e., the thermal insulation of the rectangular block is ensured). The geothermal gradient is taken as the lower boundary condition. The geological and palaeogeographical models were created as data sources for input parameters for modeling.

The geological model is a general geological section containing a few layers down to 5 km deep. The porosity, water content, thermal physical properties, temperature of beginning of freezing and other parameters were defined for every layer according to data from V.V. Kondakov (Kondakov *et al*., 2011). We use also the same data from other places of Yamal Peninsula as there are no real data about ground properties for STGF.

Palaeogeographical model provides the inputs for the upper boundary conditions. Climatic and sea level changes, existence and thickness of cover glaciations were the main content of the model. Palaeogeographical changes in the STGF area and over the whole northern part of the Western Siberia are the main issues for correct modeling. The universally accepted theory of environmental changes in this region is not yet developed. For the purposes of modeling we undertake the palaeogeographical model on the base of numerous open publications and author`s experience which consider the cover glaciations and relevant glacioisostatic sea level changes for this area (Fig. 1). The modeling period was the last 230 kyr (from the end of Middle Pleistocene) according to our modeling experience for the Laptev Sea shelf (Romanovsky *et al*., 2004). We consider three glaciations periods: 200-140, 90-80 and 70-57 thousand years ago (kyr BP). Between these periods, subaerial or submarine conditions were considered over the investigated area.

The mathematical simulation includes the temperature field calculations down to 5 km deep for the last 230 kyr taking into account the geological and palaeogeographical models. Some parameters (for example thermal conductivity of the deposits or value of a heat flux) were varied during modeling to validate the model response.

We use the distinguished equilibrium curves for the different variants of modeling. The equilibrium curve is calculated for the natural gas we used for the deep productive horizons. The same curve is used for pure methane which is used for the upper permafrost horizons, where biogenic methane usually occurs (Fig.2).

Methodology of experimental modeling

Methodology of experimental modeling to study self-preservation of pore gas hydrate in thermobaric conditions, characteristic of frozen deposits of South-Tambey gas field consisted of several stages. It included:

- artificial gas hydrate saturation of sediment samples collected from the frozen horizons;
- study of the hydrate decomposition process in frozen samples after reducing gas pressure below line of three phase equilibrium (gaseous phase – gas hydrate – ice);
- self-preservation effect of porous gas hydrates is estimated under nonequilibrium conditions.

Physical modeling of gas hydrate self-preservation in pore space is conducted on the original experimental installation (Chuvilin & Kozlova, 2005; Chuvilin & Guryeva, 2009). It aims at obtaining saturation by hydrates frozen sediment samples and at studing the kinetics of dissociation of gas hydrates at temperatures below zero and reservoir pressure characteristic. The experimental instrumentation consists of a pressure chamber - a volume of about 419 cm^3, designed for pressure up to 20 MPa - thermostat for temperature control of pressure chamber, installation for conversion of electric signals of the sensors in digital and computers. Accuracy of measurement in the pressure chamber is 0,05°C and the pressure - 0,005 MPa.

The methane is used as the hydrate-forming gas, since these hydrates are the most common in shallow permafrost. The actual volume fraction of methane is 99.98% (Chuvilin & Kozlova, 2005).

The experimental matrix was sand and sandy loam, sampled from frozen horizons of the Yamal Peninsula. The characteristic of sediments is presented in the table 1.

The samples are used to create favorable conditions for saturation by gas hydrates in experiments. Their water content is about 17%. The samples prepared for the experiment have a diameter of 4.6 cm and height of 10 cm. In the pressure chamber the sediment sample are freezed and saturated with cooled methane at a pressure of 5 MPa. The accumulation of gas hydrate in the pore space of sediments is at temperatures below zero. The cyclic freezing-melting of samples at pressures above the equilibrium line is carried out for an increased accumulation of hydrates in the pore space. The calculation of transition of methane to hydrate form is conducted by varying temperature and pressure conditions in the experiments using the PVT technique with compressibility (Chuvilin & Kozlova, 2005). In this case, the main parameters of accumulation of hydrate are calculated: volume hydrate (Hv,%), hydrate saturation (Sh, %) and hydrate coefficient (Kh, u.f.) - share of pore water transforming into hydrate from the total amount of water in the sample. The hydration number of 5,9 is used to calculate main parameters of hydrate content in sediment samples.

The hydrate saturated sediment samples in pressure chamber with known parameters of hydrate content are used in the ensuing investigations of kinetics dissociation of hydrates during the decrease of gas pressure below equilibrium line. Gas pressure in the pressure chamber is reduced to the values of 0,6 – 1,3 MPa at a constant temperature below zero – 5,2°C, allowing to follow the kinetics dissociation of gas hydrates at the thermobaric conditions corresponding to gas reservoir intervals.

After dissociation damping of gas hydrates in frozen samples residual hydrate content in the sample is determined. The characteristics of residual hydrate contents are used for quantification of metastability of gas hydrate formations in the sample.. In this case, the coefficient of self-preservation (Ksc) calculated represents the ratio of the residual hydrate content of frozen sample to the value of initial hydrate content (at equilibrium conditions).

The results of mathematical modeling

The results of calculations are represented by two types of graphs reflecting temperature fields change through time. The first type of graph (Fig. 3) is the temperature fields evolution. The “zero” isoline is a boundary of cryolithozone. The second type of graph reflects the dynamics of the gas hydrate stability zone and represents the difference between model temperature field and the equilibrium temperature of the gas hydrate at a suitable pressure (Fig. 4a, b). The negative areas on the plot are related to the gas hydrate stability zone.

The results of modeling showed that thick cryolithozone formed during the glaciation period. Figure 3 shows the most authentic version of the calculations based on the accepted admissions. It helps comparing modeling results and present data. According to published data (Kondakov *et al*., 2011) in STGF the modern cryolithozone thickness is 500-550 meters and ground temperature is about 50°C at the depth of 2 km (Skorobogatov *et al.*, 2003). During the aggradation periods of cryolithozone,its thickness was more than 600 meters. During marine transgressions, usually following glaciation, the permafrost partially degraded mainly due to thawing from the bottom. The GHSZ formed mainly under glaciers due to low temperatures and additional pressure, and its thickness could reach the depths of 1 km or more (Fig.4). In the warming periods the GHSZ degraded. Thus degradation has been slower during marine transgressions than during subaerial periods, because the additional pressure of marine’s water remained. The comparison of figures 4a and 4b shows the difference of GHSZ for gases with specific contents. The evolution of the lower boundary of GHSZ is presented in fig. 4a while the evolution of the upper boundary is presented in fig. 4b. The analysis of the figures allows finding the stages of geological history during which the GHSZ was located near the surface within the permafrost and bottom parts of glaciers. Until now the permafrost has not thawed completely, due to the presence of relic gas hydrates near the earth`s surface in a metastable condition is possible.

The results of experimental modeling

After artificial saturation of porous sediments by gas hydrate in a pressure chamber, frozen samples with high maintenance of gas hydrates are obtained. In equilibrium conditions (before pressure decrease) the saturation of hydrates in sand samples reached 54%, and in sandy loam - about 34%. Thus about 50% of interstitial water in samples was transformed to a gas hydrate form. Further frozen hydrate-saturated samples were investigated under nonequilibrium conditions. For this purpose, gas pressure in a pressure chamber with the sand sample decreased to 1,3 MPa, and for the sandy loam to 0,6 MPa at temperatures -5,2°C. This negative temperature is similar to natural temperatures of gas-yielding horizons. Experimental studies of kinetics dissociation of gas hydrates in frozen samples take not less than 10 days. Results of self-preservation studies of gas hydrates in frozen samples under nonequilibrium conditions are presented in fig. 5 and in table 2.

Analysis of dissociation kinetics of gas hydrate in frozen sediments at a pressure below equilibrium shows that after pressure decrease hydrates rapidly decompose. Over time, the intensity of decomposition decreases, and eventually almost stops (Fig. 5). This is due to the manifestation of the self-preservation effect of gas hydrates. Its essence is to form around the particles, a decomposing gas hydrate ice film. It is formed from supercooled water phase, which occurs during hydrate surface decomposition under freezing temperatures (Ershov *et al.*, 1991, Istomin *et al.*, 2006). The comparison of hydrate dissociation kinetics for sand and sandy loam shows that in sandy loam initial dissociation is more intense than in sand. However, attenuation of the dissociation is also quicker in sandy loam than in sand. Self-preservation of gas hydrates is affected by many factors such as the magnitude of investigated pressure, the permeability of the sample, and macro and micro morphology of the hydrates (Chuvilin *et al*., 2011). As a result of self-preservation effect, undecomposed gas hydrate may be in a metastable state for a long time (Ershov *et al.*, 1991, Chuvilin *et al*., 1998). By the end of experiments the residual gas hydrate saturation of sediment samples was 9-15% (Table 2). Experiments have shown that percentage of self-preservation, which characterizes the surviving fraction of methane hydrate at lower pressures, is 26-27 %. Calculations which were carried out on experimental data show that volume of free methane can be released during melting of preserved hydrates and can reach 12-17 m^3 in 1m^3 of frozen deposits.

Considering high natural water content (ice content) of experimental sediments, and also much lower gas permeability of permafrost deposits, it is possible to expect that stability of gas hydrates formations will be higher under nonequilibrium conditions in permafrost deposits.

In general, conducted experimental investigations suggest the possibility of self-preservation of gas hydrate in permafrost horizons within the South Tambey area and existence of relict gas hydrates there.

Discussion

The results of mathematical modeling show that there were periods when the GHSZ started from the ground surface in the geological past (Fig. 4, Fig. 5). Such conditions occurred during the glaciations in the middle of the Late Pleistocene. Subsequently stable zone of gas hydrates partially degraded with permafrost but did not fully disappear. The maximum depth of the top of GHSZ to 200 m was estimated about 50-40 kyr ago. Probably some of gas hydrates formations could remain into metastable state. At the end of the Late Pleistocene, they again fell into a zone of stability, which reached almost the ground surface. Only in the Holocene the top of GHSZ again sank to a depth of about 150 m.

As shown by the experimental investigation lowering the top of GHSZ in permafrost should not be accompanied by fast decaying of interpermafrost gas hydrates. There is an attenuation of gas hydrates dissociation and the formation in permafrost of metastable (relic) gas hydrates due to self-preservation process at the temperature below zero. According to thermodynamic calculations, the half-cycle of frozen gas hydrates at non-equilibrium conditions (pressure 0.1 MPa) strongly depends on the size of gas hydrate‘s particles. Thus, with increasing size of gas hydrate‘s particles from 10 micron to 1 mm, the time of half-cycle of gas hydrate is increased to 10000 of times (Uchida *et al*., 2011).

According to our estimates, in favorable permafrost-geological conditions (high ice content of permafrost, low negative temperatures, no thawing and mass transfer processes) the relic gas hydrates in upper horizons of permafrost can be remain for thousands of years.

Conclusion

Our research suggest that at the present time in permafrost horizons within South-Tambey gas field relict methane gas hydrates can potentially occur at depths of 150-200 m and deeper into the GHSZ – as interpermafrost and subpermafrost gas hydrates formations with more complex composition. Relict gas hydrate formations in the frozen sediments are characterized by high sensitivity to thermal and chemical effects. Rising of temperatures and melting hydrate-bearing frozen sediments in metastable state due to self-preservation effect, will be accompanied by an active dissociation of gas hydrates and methane emissions. These mathematical and experimental modelings were performed on Yamal peninsula with parameters from South Tambey field. But this situation, with shallow gas inside the permafrost is not a specificity of Yamal. Other Arctic areas which have been under similar glacio-eustatic and PVT changes could also contain shallow relic gas hydrates.

Acknowledgments
This work is performed within a collaboration between SOI, MSU and Total. The authors thank the different organizations for authorization of publication. They also thank S. Ogorodov, M. Sacleux, C. Channelliere, P. Lattes, J-B. Geldof for fruitfull discussions.

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Table 1. Characteristics of sediments

Type of sediment	The content of particles in each fraction,%			The mineral composition,%	Salinity, %
	1-0.05 mm	0.05 - 0.005 mm	<0.005 mm		
Sand	89,9	6,1	4,0	Quartz - 93,7	0,068
Sandy loam	59,9	28,9	11,2	Quartz - 59,5 Albite - 22,0 Microcline -13,6	0,178

Table 2. The main characteristics of hydrate metastability in investigated samples

Type of sediments	Conditions of dissociation		Characteristics of hydrate content				K_{sp}, s.u.
			The initial (before experience)		The final (after experience)		
	P_d,MPa	T_d,°C	$S_{h\ in}$,%	$K_{h\ in}$,u.f.	$S_{h\ f}$, %	$K_{h\ f}$, u.f.	
Sand, W=17%	1,3	-5,2	54	0,51	15	0,14	0,27
Sandy loam, W=17%	0,6	-5,2	34	0,47	9	0,12	0,26

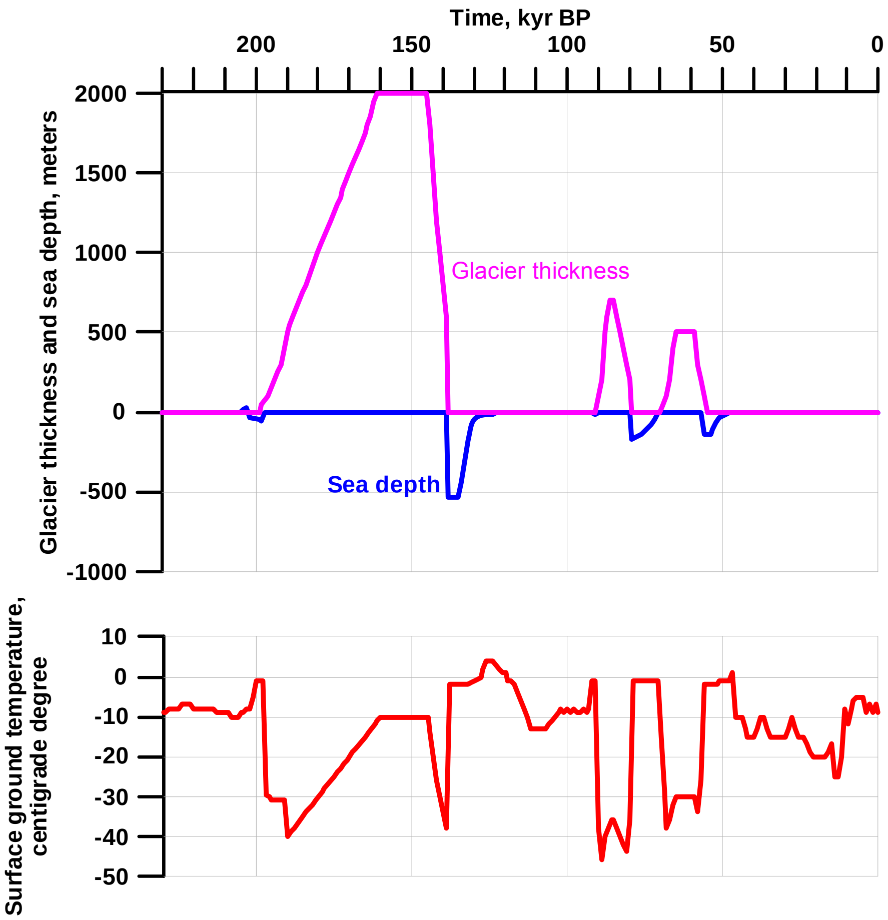

Figure 1. Environmental changes accepted for mathematical modeling.

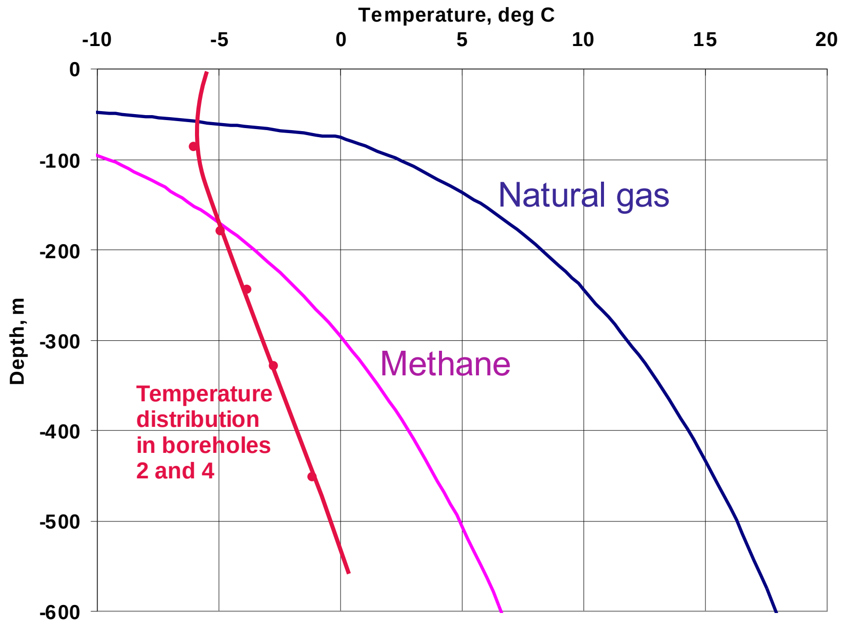

Figure 2. Equilibrium curves for natural gas and pure methane. Temperature distribution within South Tambey gas field is shown according to Kondakov et al., 2011.

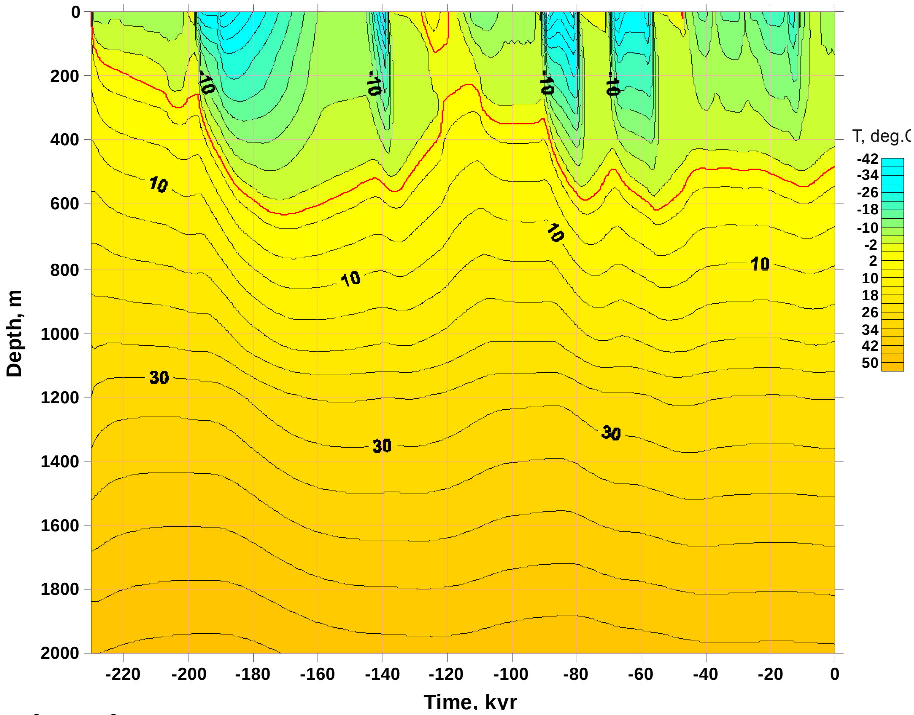

Figure 3. The evolution of permafrost.

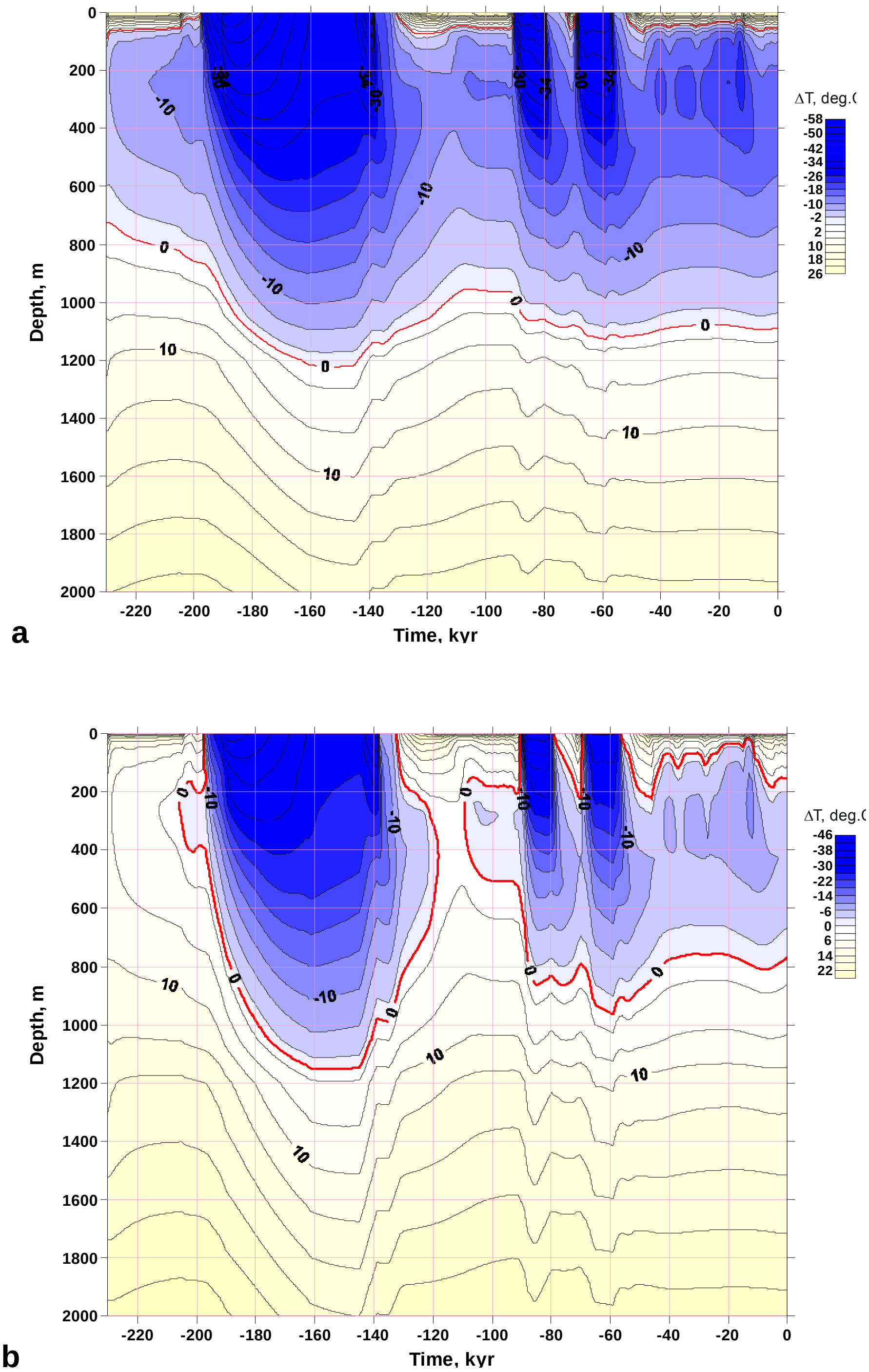

Figure 4. The evolution of gas hydrate stable zone: a - for natural gas composition, b - for pure methane.

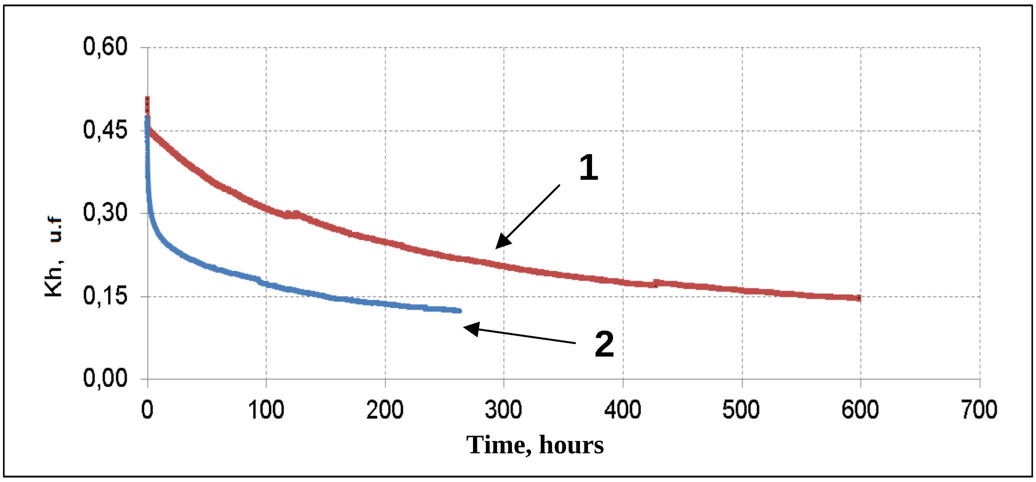

Figure 5. Dissociation kinetics of methane's hydrate in examples of the frozen artificially hydrate-saturated sediments at pressure decrease in sand to 1,3 MPa (1), sandy loams to 0,6 MPa (2) at a temperature of -5,2 °C.