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GAS HYDRATES - UNCONVENTIONAL GAS SOURCES - THEIR FORMATION, PROPERTIES, DISTRIBUTION AND GEOLOGICAL RESOURCES

An overview on gas hydrates data onshore and offshore deposits as a potential unconventional source of hydrocarbons is provided. The attention to such type of unconventional hydrocarbon resources is associated with the fact that its volume is significantly greater than the volume of other gas types. The basic properties of gas hydrates, as well as geophysical and geochemical conditions that determine the possibility of their formation and preservation in sedimentary strata are analyzed. The assessment of gas hydrates resource in Russia and in the world is presented.

Keywords: *gas hydrates, unconventional hydrocarbon source, free gas, gas fields, geological resources, mining technology.*

By the end of the XX century, the attention to the study of unconventional gas reserves has been increased due to the depletion of convention gas resources and, at the same time, the expansion of areas of their application and practical importance increasing in the global economy. Some of them, such as coal methane fields, has been developed and studied for a long time. Production of unconventional gas from other significant sources - low permeability reservoirs and shale formations - is carried out in a significant scale only in the US because of the high cost of the development technology of these resources and negative environmental consequences for areas of their development.

At the same time the study of gas hydrates, which presents the largest potential resources among unconventional gas resources was expanded, however, their overall study is one of the lowest level.

Gas hydrates are solid non-stoichiometric compounds (ie, of variable composition) of cell type - clathrates (Latin. «Clathratus» - placed in a cage). Compounds of this type have been known since 1811, when H. Davy has described a hydrate of chlorine ($Cl_2 \cdot 5.75\ H_2O$), saturating water with it at t ~ 0 °C. But the name of compounds of this type – clathrates - was given only in 1948 by Powell. Clathrate compounds generally described by the formula: $M \cdot n\ H_2O$, where M is a molecule gas, n is the number of water molecules.

Gas hydrates are formed by the inclusion of gas molecules (volatile liquid) in the frame cavity (crystal lattice) constructed by H_2O molecules in thermodynamic conditions particular for each component gas. When the conditions are not accomplished the molecules of "guests", ie gas, held in open water framed by weak Van Der Waals forces, leave it and hydrate is decomposed on gas and fresh water with a significant absorption of heat.

Clathrate frame may have cubic, tetragonal and hexagonal structures with a different number of water molecules and different size of cavities. CH_4 molecules prevailing among natural gases, fill the water frame in a regular pattern of cubic structure of types I and II.

The number and size of the cavities inside the frame of the crystal lattice of water depend on the structure and the number of H_2O molecules that created it. Thus, the cubic structure of the type I is formed by 46 molecules of H_2O and consists of 6 large and 2 small cavities, while type II is formed by 136 molecules of H_2O and consists of 8 large and 16 small cavities. The limit of the number and volume of the cavities in the lattice of water frame limits the diameter of "guests" molecules. This can be gases, the molecules diameter of which is in the range of 0.38-0.92 nm. Among them are C_1-iC_4; CH_4, N_2, H_2S, SO_2, CO_2, O_2, Ar and Xe. There are also other hydrate-forming molecules, which are not related to the natural gas, for example, volatile Cl_2, Br_2, ClO_2, etc.

Each cavity of "master", ie lattice of water frame, contains only one molecule of "guest" (gas), and they are quite different, depending on the gas composition, the temperature and pressure conditions of the environment. Thus, the molecule of methane hydrates - CH_4. 5.75 H_2O - occupies any cavity in a cubic frame, while molecular mixture of complex composition - – $CH_3C_6H_{11} \cdot 5H_2S \cdot 34\ H_2O$ - as part of the hexagonal structure needs in the large-volume cavities. Only clathrates with the most complete filling of its cavities by "guests" (> 95%) are characterized by thermodynamically stability.

H_2, He, Ne, n-C_4 and C_{5+upp} do not transfer in the hydrate state. Helium can easily penetrate into the hydrate structure, but only in trace amounts, as an free impurity, as it cannot give compounds with H_2O because of its absolute inertness, i.e. it is not held in the cavities of the water lattice frame by Van Der Waals forces, and just as easy leave them, as enter. As a result gas-chemical abnormalities occur in the deposits of free gas of multicomponent composition in hydrate formation zone. These anomalies represent search value. The appearance of gas-producing strata of clear geochemical anomalies in such objects within limited areas (increase in helium concentration, reduction of CH_4 content) are considered as areas covered by the process of gas hydrate formations.

The physical properties of gas hydrates. Frame of water molecules of methane hydrate of cubic structure is similar to ice in many properties. Its density varies within 0.908-0.917 g/cm^3 depending on the type of gas hydrates structure and filling of its cavities with CH_4. To compare - the hexagonal structure of ice is characterized by a density of 0.912 g/cm3. Many physical and mechanical properties are also similar - Young's, Poisson modulus, as well as the speed of sound, electrical and thermal properties. In particular, gas hydrates cement the rocks like ice and markedly increase their mechanical strength.

Table 1 and 2 show the values of the main indicators related to the physical properties of gas hydrates that are necessary to simulate the conditions of their existence in nature and diagnostics.

The heat of phase transitions of methane hydrates into gas and water is almost 1.5 times higher than the transition of ice into water. Thermal conductivity of methane monohydrate is almost 4 times smaller than the thermal conductivity of ice. The thermal conductivity of hydrate-saturated soil is only twice less than the thermal conductivity of frozen soil (data of E.D. Sloan, 1998). The value of the statistical dielectric constant of hydrates is close to 58 (Table 1), while of ice - 80.

Table 1

Mechanical and electrical properties of gas hydrates

Properties	Gas hydrates	
	sI	sII
The unit cell parameters at 273.15 K, nm	*a* = 1.197-1.215	*a* = 1,714-1.757
The number of water molecules per unit cell	46	136
Crystallographic density of frame, g/cm^3	0.796	0.782
The volumetric thermal expansion, K^{-1}	$(1.5\text{-}1.7)x10^{-4}$ (evaluated)	$(1.5\text{-}1.7)x10^{-4}$ (evaluated)
Isothermal Young's modulus at 268 K, MPa	$8.4x10^3$ (evaluated)	$7.2x10^3$ (evaluated)
Poisson modulus	≈ 0.3	
Speed of sound (longitudinal propagation) at 273.15 K, km/sec	3.5-3.8	
The static dielectric constant at 273.15 K	≈ 58	
High-frequency dielectric constant at 273 K	3.4 (evaluated)	
Thermal conductivity coefficient at 273 K, W/(m•K)	0.5	

Table 2

The enthalpy of dissociation of methane hydrates and the individual homologues

Hydrate	Dissociation enthalpy ΔH, kJ / mol	
	Into gas and water	Into gas and ice
$CH_4 \cdot 6\ H_2O$	54.19 ± 0.28	18.13 ± 0.27
$C_2H_6 \cdot 7{,}67\ H_2O$	71.80 ± 0.38	25.70 ± 0.37
$C_3H_8 \cdot 17\ H_2O$	129.2 ± 0.40	27.00 ± 0.33
$C_4H_{10} \cdot 17\ H_2O$	133.2 ± 0.30	31.07 ± 0.20

Different values of gas content in methane hydrates during its decomposition is frequently presented in the literature - 130-186 m^3/m^3, this may be caused by the study of gas hydrate systems of incomplete filling of "master" structure by "guests" or heterogeneity. Specific gas content of CH_4 during complete filling of gas hydrate cavities of cubic structure of I type with a density of 0.916 g/cm^3 during decomposition is estimated to 170.6 m^3.

Thermodynamic stability of gas hydrates is a basic condition for the formation and preservation of hydrates and, respectively, an important criterion to identify areas of possible gas hydrate formation. Changing of thermodynamic conditions in the system leads to decomposition of hydrates. The main parameters of strata, which must be characterized for allocation of possible gas hydrate formation, are the following: temperature, pressure, gas composition and groundwater mineralization, as well as lithofacial composition respectively (permeability) of the strata.

The graph on Fig. 1 characterizes the thermodynamic conditions of hydrate formation for natural gas that most common in the subsoil. As the graph shows, CH_4, CO_2 and H_2S easily move in the hydrated state. Transition of N_2 is considerably more difficult, it requires a lower temperature, or high pressure. The combination of low temperatures and high pressures in the interior is typical only for cryolithozone, so zones of gas hydrates formation in the sediments of the land are confined to areas of "permafrost".

As a result of differences in the values of the physical parameters required for the formation of hydrates from the individual gas components the fractionation of composition of multicomponent natural gases occurs in hydrates and residual free gas in areas of possible gas hydrate formation. Therefore, the wider the diversity of natural gas composition, the more difficult to determine the actual border line of the areas of possible gas hydrate formation. Moreover, the clathrate lattice frame is constructed only of H_2O molecules without mineral components; during intense gas hydrate formation changes not only the composition of the gas, but also groundwater mineralization. If areas of increased mineralization of groundwater, with similar chemical composition or accumulation of free gases with higher helium content appear in the zones of hindered water exchange in the strata of the areas of possible gas hydrate formation, it is possible to assume that in this area the gas hydrate formations has occurred already in the past or is currently taking place.

High mineralization of groundwater is not only slow down, but sometimes excludes the possibility of gas hydrate formation as cavities of water lattice frame are occupied by salt molecules. This is the case in Russia in petroleum provinces of the Eastern Siberia, where the mineralization of groundwater of chloride calcium composition reaches in some regions 300-400 g/kg, with a high content of $CaCl_2$. It is generally known that the concentration of $CaCl_2$ in the range 25-35% (wt) is an active inhibitor of man-made gas hydrate formation and is widely used in oil and gas practice to prevent it. High anti-hydrate activity of reservoir waters of Eastern Siberia, as in the whole their high mineralization makes difficult and sometimes even eliminates the possibility of gas hydrate formation. In the fields of Western Siberia, where the groundwater mineralization is relatively low ~15-30 g/l, the processes of man-made (and not only) hydrate formation in the oil fields are very active. We also note that natural groundwater mineralization, exceeding 100 g/l, lowers equilibrium temperature of hydrate formation at 5-12 °C.

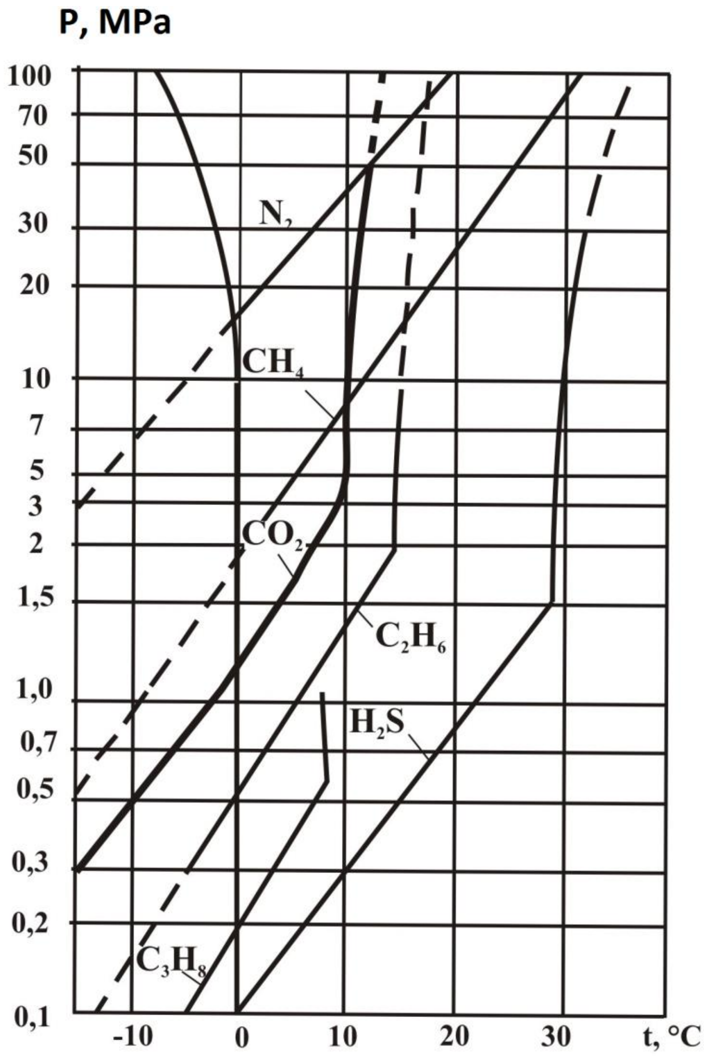

Fig. 1. Equilibrium thermobaric conditions of hydrate formation for individual gases
[Makogon, Fomina, 1980]

We should stop at another factor of influence on the gas hydrate formation processes in the interior - lithofacial composition of gas producing rocks. Studies carried out by V.S. Yakushev [Yakushev, 2009] showed that the activity of gas hydrate formation processes in the interior varies in any direction, and even stops depending on the degree of permeability of deposits. The most favorable conditions for formation and accumulation of gas hydrates are highly permeable pure fine-grained sand. With increasing impurity of clay particles the variations in the thermodynamic parameter of gas hydrate formation increase. In heavy clay, the lower the humidity (< 10% vol.), the less likely the gas hydrate formation, as water film, as well as capillary and osmotic water in these processes does not take part. But in these heavy clays with high humidity (> 80% vol.)

hydrate formation occurs under milder thermodynamic conditions in comparison with the equilibrium.

Thus, it is important to emphasize that the intervals of boundaries of areas of possible gas hydrate formation in vivo subsoil are mobile and when forecasting them it is necessary to assess not only the thermodynamic parameters of environment, but also compositions, the amount of water and gas and their mobility in the depths, ie rock permeability, providing continuity to upgrade gas-water contact for the full implementation of gas hydrate formation processes.

Here is an example of visual observation of the gas hydrates formation in a condition of movable contacts of gas and water based on the foreign press about the crash on the DH platform in Gulf of Mexico on Maconda Prospect deepwater oil field with reserves of 100 million barrel (20th April, 2010). "After the explosion at the well head, high-pressure gas (> 88 bar) reached the platform. Geyser up to 70 m gushes at the top of the derrick. Snow-like flakes rained down, steaming from the evaporation of methane". Directly during the disaster no one has studied this process, since the period from explosion at the well to the fire on the platform took only 2 minutes, but it is obvious that the "snow" is methane hydrates with homologs formed in turbulent blowouts of gas, oil and water under conditions of drastically reduced temperature due to sudden adiabatic expansion of gas, with absorption of heat. Subsequently powerful hydrate formation near the mouth of the well (at a depth of 1.57 km) made it difficult to eliminate the accidents (1.5 km depth of the bay, 3.9 km depth of downhole, reservoir pressure of about 600 atmospheres).

Almost the same processes, but in the natural, not man-made environment, take place during emissions of underwater mud volcanoes, forming various scale fields of methane hydrates on the bottom around the crater of a mud volcano.

Methods for detection of gas hydrates. Reliable information on the presence of gas hydrates in subsoil provide only direct methods, ie their visual observation in cores from boreholes or bottom sampler (gravity pipes and so on) extracted from areas of possible gas hydrate formation. All the rest methods used to search for gas hydrates (geochemical and geophysical) are indirect. The vast majority of manifestations recorded as gas hydrates in the subaqueous conditions are indirect and it is only in objects with relatively high hydrate-saturated deposits - 20-30%, their presence becomes persuasive.

Geophysical methods are widely used in the practice of search of gas hydrates as the most developed and affordable, especially in the waters. However, due to informativeness they often remain indirect methods. They are based on significant differences of physical properties of the gas, water, and gas hydrates. On the other hand, the similarity of some properties of gas hydrates to the properties of ice hinders their differentiation, especially if simultaneously all three phases present in the sediments - solid, liquid and gas in close volumes. In such objects the reliability of geophysical methods is significantly reduced. In addition, the bulk of gas hydrates is present in areas of possible gas hydrate formation in the form of accessory inclusions of different shapes, or a needle-like nodules and thin layers in the thickness of dispersed rocks of different composition and structure, i.e, small, scattered accumulations.

If the volumes of gas hydrates do not exceed 10-15% of the surrounding rocks, their detection by geophysical methods is unlikely.

Monohydrates with an admixture of terrigenous material no more than 5-10% are surely geophysically diagnosed. Samples with an admixture of gas hydrates more than 40% are likely to be geophysically diagnosed in case of the absence of ice in them.

The electric logging (resistivity, spontaneous polarization, etc.), varieties of radioactive logging and seismoacoustics are applied to identify gas hydrates. The most significant sign of the possible presence of gas hydrates under the bottom waters in areas of possible gas hydrate formation is the presence of BSR (*Botton Simulating Reflectors*) - «false bottom reflection» on the seismic profiles reflector and all sorts of anomalies in the acoustic profiles in the form of alternating dark and light triangles, "pagoda" and "bright spots" (*VAMP's - velocity amplitude features*), the formation of which is associated with the presence of gas hydrates, given their spatial coincidence with areas of possible gas hydrate formation (see Fig. 1). The presence of gas hydrates in them is sometimes confirmed by drilling results, but not always. Therefore, other reasons for their formation were discussed, mainly related to the diagenesis of bottom sediments and geochemical processes in them, altering their physical properties, and even defect of the method of focusing of acoustic signal on uneven seabed and so forth. There have been inverse surveillance - no anomalies on seismic profiles and the presence of gas hydrates in the drill core (samplers). Despite the difficulties in interpreting the results of acoustic methods they are now widely used in practice to identify gas hydrates in the sediments on the basis of frequent coincidence signals of BSR and VAMP's with zones of thermodynamically favorable gas hydrate formation, especially with high gas saturation of bottom sediments (free, in the form of dispersed gas bubbles) with a very moderate mineralization (35 g/l), saturating them by marine waters and weak seal of deposits.

Some of geophysical methods during well logging for rock penetration in areas of possible gas hydrate formation with interlayers of comparatively pure hydrate (<10-15% of impurities) are relatively reliable, subject to certain limitations in drilling technology (using of cold drilling muds and inhibitors with gas logging, etc.).

Geochemical methods to identify gas hydrates are based primarily on differences in the chemical composition of natural gas and hydrate forming properties as well as in the degree of groundwater mineralization in areas of possible gas hydrate formation. Since not all natural gases form gas hydrates, and hydrate lattice is constructed by H_2O molecules, without participation of minerals dissolved in the groundwater, it is obvious that the local gas-hydro-chemical anomalies will inevitably arise during intense gas hydrate formations. For instance, residual free gas will be enriched by neon, helium, and higher homologues of methane and will also lose a significant portion of CH_4 from natural gas, as well as gases (CO_2, H_2S, etc.) that easily pass into hydrate state. At the same time, the mineralization of residual groundwater will increase, while overall composition will stay the same, and the composition of gas will change with respect to groundwater.

However, geochemical methods, as well as geophysical and not always correct. Thus, the reduced groundwater mineralization may be associated with dehydration of clay minerals, but not with the process of gas hydrate formation.

Isotopic techniques are rarely used due to hardware complexity and high cost of analyzes. $\delta^{13}C$ of methane is especially informative for substantiation of gas source - catagenic (~ -35 ‰) and biogenic (-75 ‰).

The geological characteristics of gas hydrates. The presence of gas hydrates in the core samples from areas of possible gas hydrate formation in a sealed sampler can be estimated by the excess volume of free gas released from the container, compared with capacitive capabilities of the core and the container during cooling of the walls of the container and the sample, as the decomposition of gas hydrates is accompanied by the loss of heat (adiabatic expansion of gas). Also, the bubbling surface of the core in the sampler can be observed during rapid rise of deposit sample, as well as the squeezing out of the sediment from corer due to excessive increase of pressure therein caused by produced free gas during the decomposition of gas hydrates.

If the deposits are cemented by gas hydrates, like frost, than the penetration rate decreases during drilling due to increasing in the density of rocks. When using hot drilling mud the caverns are formed in the borehole and intense gassing of liquid mud is observed from a depth not conforming to the possibility of high gas saturation of the subsoil. When penetrating wells with a cold mud these phenomena are not observed. They are also not observed when hydrates are identified, but their proportion does not exceed 10-15%.

Gas hydrates in the permafrost. The need for the study of this phenomenon is associated with many cases of accidents - explosions, fires, emissions of during mud during drilling of permafrost rocks, widespread not only in the Arctic region of the planet, but also in much southern regions, such as in Eastern Siberia (Lena-Tunguska petroleum province). In some places the thickness of permafrost rocks reaches 500-600 m, rocks are cemented by ice, i.e. practically impermeable. There are no reservoirs for gas accumulation formation, however, there is no other explanation for the accidents, but the gas explosions. It should be also noted that in some cases, these gas manifestations were observed above the area of the upper boundary of the permafrost zone up to the surface in case of maintaining the negative temperatures, i.e. out of taliks zones and so on.

Research of physical and chemical bases of formation of the different states of natural gas in the interior, including gas hydrates under freezing temperatures, made by V.S. Yakushev [Yakushev, 2009], as well as the experimental works and field studies carried out by him, have shown the ability of gas hydrate to self-preservation. The essence of the effect is that during the value of the pressure in the permafrost rocks below the equilibrium for areas of possible gas hydrate formation (inversion on land or regression of the sea level) the previously formed accumulations of gas hydrates are decomposed, but while maintaining a negative temperature in the permafrost rocks the fresh water on their surface freezes, covering gas hydrate by ice armor and protecting it from further degradation. The future of such "preserved" gas hydrate depends on thermobaric stability of subsoil in geological time and the structure of hydrate themselves.

Such kind of cores (sandy loam and loam) with icy gas hydrate accumulations were extracted from wells drilled at the Bovanenkovo and Yamburg fields (Yamal peninsula, Russia) in the Quaternary sediments at depths from 30 m up to 110-130 m, i.e. significantly above the upper limit of areas of possible gas hydrate formation.

The chemical composition of the gas produced from decomposed gas hydrate is close to the biogenic gas - 91-92% methane, 8-9% nitrogen. Many frozen rock samples were obtained from the sandy layers of Quaternary deposits.

Catastrophic gas manifestations during drilling in the permafrost rocks probably have to be associated with the presence of pockets with free "relic" gas, which is not transformed completely into hydrate due to a shortage of free water in the permafrost, because the decomposition of hydrates during the opening of the well is a slow energy-intensive process, rather than explosive, i.e. time is needed for hydrate decomposition and accumulation of gas in sufficient volume for the implementation of emergency processes.

The conclusion that can be drawn from the data obtained by V.S. Yakushev [Yakushev, 2009] is that the self-preservation of gas hydrates in permafrost, and their preservation in a relict state is a widespread phenomenon in areas of permafrost and it should be taken into account when assessing the extent of the geological resources of gas hydrates, in addition to those recorded in areas of possible gas hydrate formation. However, we can associate their presence with catastrophic gas manifestations during drilling of permafrost rocks with huge gas flow rates up to 10 - 14 thousand m^3 per day only in case of presence of free gas pockets, migrated from the depths and not transformed into gas hydrate state because of a shortage of free water in the permafrost.

Distribution of gas hydrates and their main areas of concentration. Considering the whole gas productivity of subsoil and conditions of stability in the distribution of zones of hydrate formation, we can distinguish two basic planetary blocks - continental and aquatic, where the identification of gas hydrate stability zone can take place.

Distribution of gas hydrate is very broad, but mostly scattered. They are found everywhere in the subsoil, where there is gas, water with moderate mineralization and thermobaric conditions corresponding to stability of the gas hydrate formations. Approximately 10-20% of the cold bowels on the continents include areas of permafrost, and 80-90% of water areas in the shelf and continental slope satisfy the conditions of gas hydrate formation.

Considering the overall gas productivity of subsoil and focusing mainly on the linear nature of the temperature and pressure distribution in most regions of the Earth, as well as the confinement of the equilibrium conditions of hydrate formation stability to the upper floors of the sedimentary cover, both on land and in waters, with relatively mild temperatures (-5 - 15° C) and pressures (up to 100 MPa), the two main blocks of planetary regions can be distinguished - continental and aquatic, where the reality of formation of gas hydrate stability zones is confirmed by the calculations based on circumstantial evidence and direct by findings in core or samplers.

Continental block includes gas productive sedimentary cover within the Arctic land, together with the coastal shallow waters (up to 100 m), as well as areas with strong cryolithozone (< 300 m) with slightly different thermodynamic parameters for areas of possible gas hydrate formation.

Gas hydrates are formed and accumulated in deposits of gas fields that are wholly or partly belong to areas of possible gas hydrate formation and in thickness of permafrost rocks and beneath their bottom in the small gas accumulations. In deposits with commercial reserves of free gas located in areas of thermobaric stability, the gas hydrates are accumulated mainly in water-gas contacts, forming a sort of "snow" ghosting along the contours of deposit, well allocated by geophysical methods. They are also formed in the interior, flooded parts of deposits - lenses, streaks, etc., not only in gas deposits, but also oil in case of their high gas saturation. Free gas of deposits in its main volume does not pass in solid hydrate state in areas of possible gas hydrate formation, due to the shortage of free water in the pores of the reservoirs, occupied by gas. The fixed (film) water does not take part in the processes of hydrate formation, it is firmly held by rock. Gas hydrates have been identified in many core samples during drilling in gas fields in the Arctic slope of the North American continent in Alaska and Canada (Prudhoe Bay, Kupa-Ruk, Malik et al.).

In Russia, the level of study of the distribution of gas hydrates in subsoil of the land is low, not so much because of the lack of interest, but due to the fact that the top of the absolute majority of the identified gas deposits even in the polar regions of the country are located deeper than estimated bottom of areas of possible gas hydrate formation, example – under-Cenomanian deposits of Yamal.

Messoyakha field in Western Siberia was considered as a gas field with gas hydrates defined by indirect signs (geophysical and geochemical) in Russia. There were even suggestions on individual share of gas hydrates in gas supply of Norilsk - 2 of 9 billion m^3 of gas was allegedly submitted to the consumer due to the decomposition of gas hydrates, after reducing the pressure in deposit during gas production. Studies carried out by the "VNIIOkeangeologia" institute [Ginzburg, Soloviev, 1995] to determine the evidence of gas hydrates in the same field, have not confirmed their presence, but does not exclude the possibility of their presence at an earlier stage of field development on the basis of helium anomalies in the residual gas although not in such scale that noted above.

Gas-producing deposits under a thick layer of permafrost, developed in the Asian part of Russia far to the south of Eastern Siberia can be referred to the territory of a possible accumulation of gas hydrates in the continent in Russia. Permafrost covers about 60% of the territory of Russia and most of the vast territory of the Siberian platform.

Its section, even in the southern gas-producing regions is 500-600 m (Nepa-Botuoba anteclise), while in the central part of the platform it reaches 1.5-2.0 km. Following the bottom of permafrost with its temperatures close to 0 ° C and even sub-zero, the whole area of a possible gas hydrate formations is lowering, but only within zones with mineralized waters.

The thickness of the permafrost rocks was not considered for a long time as containing gas hydrates, due to the absence of the reservoirs and the dubious opportunity of migration processes. However, numerous cases of emergencies during drilling in the upper (30-50 m and deeper) parts of frozen deposits demanded explanation - explosions, fires, gas and drilling fluids emissions.

As discussed above, V.S. Yakushev [Yakushev, 2009] have shown that if the gas accumulated in the sediments in the previous pre-glacial period, then during cold weather and freezing of water and, accordingly, its desalination, it could go into the solid hydrate state and be preserved in permafrost rocks. During mitigation of thermobaric conditions (warming, inversion with erosion, ie reducing the pressure) gas hydrate, starting to decompose, is covered by ice from the water released in the beginning of its decay in areas with below zero temperatures in the permafrost. Its decomposition under the ice shell is terminated and gas hydrate is self-preserved in the permafrost indefinitely. Relict hydrates saturate permafrost rocks in many regions with cryolithozone provoking alarm events during drilling. These processes of conservation of gas hydrates apparently took place in Eastern Siberia, which was inevitably provoked by the climate stability of the region, commonly known as a continental "cold pole" of the planet (Verkhoyansk city), as well as an inversion of platform with erosion with reduced pressure.

Similar processes are observed in the north of Western Siberia. According to calculations the bottom of the area of thermodynamic stability of gas hydrates in the Nadym-Pur-Taz region - 730 m is significantly higher than the top of Cenomanian 900-1000 m - the main gas-bearing complex in the region. The thickness of permafrost zone in the region is 350-500 m. The signs of gas hydrates in the Cenomanian was not fixed, but there were numerous emergencies during drilling in above-Cenomanian deposits. Studies executed by S.A. Leonov have shown that the bottom of cryolithozone in Yamburg field reaches 400 m, while ZVGO is in the depth interval 260-730 m. Intense but rapidly decaying gas shows observed during drilling of well at a depth of 60-200 m. In particular during drilling in the Aneryakha area not only the degassing of the drilling mud were noted, but its emissions to a height of 6 meters with a volume of rinse water up to 120 m^3. The most intense gas shows were observed from the sands of Tibeysalinsk continental sub-formation, with a thickness of 20 m at depths of 400-550 m, i.e. directly beneath the cryolithozone in areas of possible gas hydrate formation.

State of study of gas hydrates distribution in the depths of Russian land is humble. Initially the territories of possible hydrate formation include not only the subsoil of the petroleum provinces in the Arctic, but also the subsoil under powerful permafrost, that is, virtually the entire southern part of the Siberian platform. The latest studies have shown that because gas hydrates are formed only with fresh (poorly mineralized) water, petroleum provinces with calcium chloride brine in subpermafrost should be excluded from areas of possible gas hydrate formation. Thus, the main gas producing part of the subsoil of extensive cold Lena-Tunguska petroleum province with a mineralization of water of calcium chloride type up to 300-500 g/l, should not be included in the list of areas of possible subpermafrost gas hydrate formations. We also note that the technical solutions of $CaCl_2$, i. e. analogs of natural brines of eastern Siberia, are used as inhibitors for the cleanup of hydrate wells during gas production.

Unique discovery of gas hydrates in the continental part of Russia was made in 2009 with the help of apparatus "Mir-2". At the bottom of a freshwater Baikal lake at a depth of 2.4 km above the lake bottom in the area of mud volcano "St. Petersburg", acting as a torch of 900 m height, massive hills of gas hydrates were discovered, rising above the bottom and leaving into the thick sediment, lightly covered by unconsolidated sediments, crumbling when shocks.

According to preliminary estimates reserves of gas hydrates in the bottom of the Baikal lake are close to 1.4 trillion m^3 equivalent to the free phase.

The pieces of monohydrate have barely been gouged out from a monolithic array by manipulator. Large debris was clipped by manipulator and smaller ones were placed in a plastic container without a bottom (given the buoyancy of gas hydrates in water) with small holes in the top for the gas outlet. As the lifting of device the thermobaric environmental conditions changed and at a depth of 150 m the large fragment of gas hydrates clamped in the manipulator began to fall apart. The largest of its fragments, overtaking the machine, sailed up, while small parts left behind, highlighting the wisps of gas. At a depth of 106 m small hydrate fragments remaining in the container began to aerate the bottom, i.e. nondecomposed residues were in anhydrous gaseous environment on a special substrate. They freezed and were brought to the surface and placed in the freezer at -180 °C for further studies.

Baikal gas hydrates are unique and it is a highly interesting object for research, but definitely not for the development as a source of gas feed for environmental reasons. Assessing gas hydrate study of the continental land of Russia and its waters, it should be noted that it is still too low, but the evidence of widespread gas hydrates, especially in subaqueous environment of the Arctic and northern Pacific coasts is beyond doubt.

Conditions of formation of gas hydrates is ideal here - a dynamic methane continuously supplied by mud volcano, fresh water, low temperatures (3-4 °C) and high pressure (about 100 bar).

A variety of conditions in the subsoil do not allow to name specific thermodynamic parameters for marginal conditions of gas hydrate formations in free gas accumulations (deposits), they can be defined only for specific objects. Note for example, that at 10 °C and all other favorable conditions methane hydrates can be formed at a depth of 700-800 m in gas producing formation.

Aquatic block includes the waters of the continental shelves, along with arrays of collapse sediments on continental slopes and submarine landslides, as well as inland seas and deep lakes. These objects are almost universally characterized by favorable thermobaric conditions for the stability of gas hydrates (excluding shallow water without permafrost zone), and constantly renewed, significant amounts of hydrate forming gases - CH_4, CO_2 and H_2S and low-mineralized water - ‰.

According to sources of gases, conditions of formation and accumulation the subaqueous gas hydrates are clearly divided into gas hydrates in the bottom sediments and in gas deposits in the deeper subsoil - catagenic analogs to deposits on land. The leaders on a global scale in terms of distribution and accumulation of methane hydrates and variety of their forms are bottom sediments of shelves and slopes, especially in seismically active regions. The source of gas for them is mainly biogenic methane, as well as catagenic, migrating from the depths along tectonic dislocations and mud volcanoes. This deep gas forms in the bottom sediments and on the surface the largest accumulations of monohydrate, almost without terrigenous impurities.

Huge bottom area of deepwater (> 5.0 km) hypabyssal platform of the World Ocean with the thickness of deposits less than 500 m is virtually excluded from areas of possible gas hydrate formation. Deep silts and clays are presented in their bottom sediments mainly by thickness from a few tens of centimeters, rarely a few meters, are depleted by organic matter and virtually non gas-bearing, i. e. they do not have the main component of gas hydrate - methane in sufficient volume.

The average content of organic carbon in the deep areas of the World Ocean (> 3 km) is approximately 0.10%, in the marginal areas – 0.41-0.50%, on the continental slopes and in areas of collapses of shelf deposits - 0.74%. If we take into account that the nearer the continent the more the thickness of deposits, organic carbon content there, and the temperature, i. e. the bigger the total amount of organic matter and the faster its degradation and generation of CH_4, than it is obvious that in the deep parts of the World Ocean compared to the continental shelf there are no significant gas hydrate formation and accumulation, although there are sporadic discoveries of gas hydrates in the World Ocean at great depths.

The level of study of gas hydrates of the World Ocean is poor, because the fact that it holds 70.8% of area of the Earth that is the least accessible for the research. The arctic slopes of North America - Alaska, alluvial fan delta of deposits of McKenzie River in the Beaufort Sea, the Arctic archipelago of Canada and Blake Ridge (Atlantic, southeastern US) are comparatively well studied. The study of gas hydrates was especially active in 80-90-th of the last century by the United States and Canada, in cooperation with other countries on the basis of intergovernmental agreements. The research results were published widely and are summarized as on 1994 in the monograph "Submarine gas hydrates" [Ginzburg, Soloviev, 1995].

Now the coastal margins of almost all continents and inland seas are investigated for gas hydrate content with varying degrees. Major discoveries of gas hydrates in the cores were obtained in most of the seas under a layer of bottom sediment on the depth of at least 30-50 cm in the form of thin layers and sediments cemented by hydrate.

There is another, perhaps significant, but very poorly studied reserve of natural gas resources in the form of gas hydrates. It is associated with the seismic moving waters - core or solid monohydrate, confined to the faults and the channels of inflow of deep catagenetic methane in areas of tectonic activity (subduction, spreading) of the oceanic crust. Near active continental margins, island arc structures and other large modern gas-conducting permeable systems the gas hydrate accumulations with thickness of a few meters, similar to the cores extracted by the well near the coast of Guatemala can be formed in the bottom sediments and uppermost sediments and may be found in the Far Eastern seas of the Pacific and Indian oceans.

Thus, in the whole the problem of the industrial significance of natural gas resources in the form of a solid component - gas hydrates - is still under solution, despite almost half a century of study.

In Russia aquatic gas hydrate formation is widely spread within the seas of the Arctic Ocean - Behring Sea, Okhotsk Sea, and Black Sea and the Caspian Sea areas. Everywhere where coastal areas were surveyed, they have been found in bottom sediments in areas of possible gas hydrate formation. The scope of gas hydrates accumulations are not big, mainly scattered accessory inclusions or thin seams in the bottom sediments. The level of study is generally poor. Relatively large underwater accumulations of gas hydrates are formed in haloes of active emissions of mud volcano, and at some distance from the top of the fan. The gas accompanying mud emissions is mainly methane, sometimes mixed with CO_2. Both on the land and on aquatic areas the mud volcanoes are observed in the areas of modern deep troughs and valleys. In Russia, they are identified in the Black, Caspian and Okhotsk Seas.

The greatest interest in terms of aquatic gas hydrates distribution is focused on the Russian Pacific coast is East Asia, including the Sea of Okhotsk.

The search for gas hydrates in the Sea of Okhotsk started in 1984 by E.V. Zakharov and S.G. Yudin. Other researchers joined later. Searches were carried out by geophysical data, bottom samplers in sediments, on the yields of methane bubbles to the surface and even visually from submersibles MIR. By 1988-1989 9 sites with bottom gas hydrates were identified. The thickness of deposits with gas hydrate according to seismic profile was estimated to 200-300 m from the bottom. Outputs of methane were confined to fault dislocations. The methane concentration was measured at the same time in the bottom water in the water column. But during all these studies, conducted over the period 1991-2006, the thickest layer of gas hydrates extracted by gravitational tube was only 35 cm.

Later, in 2003, the activation of a stream of methane bubbles was marked, the number of their outlets has increased up to 200, which was attributed to increased seismotectonic activity on Sakhalin-Hokkaido fault system in the west of the Sea of Okhotsk, confirmed by Hokkaido earthquake with a magnitude of 7 points and subsequent numerous movements of oceanic crust accompanied by an earthquake of 5-6 points in 2010-2012. At the same time the methane saturation of water at a depth of 10-12 m from the bottom has increased in 10 times (Deriugin depression).

Specific advances in the study of submarine gas hydrates have been achieved at the end of the XX century in the seas of Southeast Asia, especially in the Nankai Trough (Sea of Japan), where at a depth of 207-265 m the three sandy interlayers were opened with an average porosity of 36%, with a total thickness about 16 m, the pore space of which is filled on 80% by gas hydrates. The well is located in a subduction zone of Javanese oceanic plate under the continental. Following Japan the South Korea, China and India reported about the discoveries of gas hydrates on the seabed, mainly according to seismic data. The large accumulation of gas hydrates was delineated and confirmed by well logging and core with the length of about 1 m in Krishna-Godavari basin near the Andaman Islands in the Bay of Bengal (India) together with specialists from the US and Europe in 2006. Similar discoveries can be expected in the future in the whole vast aquatic, island territory of Japan, and South China Seas. Especially in the zone of Malay Archipelago (Indonesia folded region), located in the Javanese lithospheric plate with extremely high current seismicity, stimulating migration of deep gas. At the same time here, in the limits of the continental shelf and on the islands, more than 350 hydrocarbon fields were discovered. Therefore there is no doubt regarding broad development of intensive processes of hydrate formation here in bottom sediments in the shelf of the Pacific plate. It is possible that the region of active margin of South-East Asia and Oceania will turned to be unique on a global scale in terms of accumulation of gas hydrates and primarily aquatic monohydrates of methane. But its study is just beginning.

During assessing the overall planetary studying of gas-hydrate-potential on land and water areas, it should be noted that it is still too poor, especially in Russia, but the evidence of widespread of gas hydrates, especially in the aquatic environment of the active margin of the northern Arctic and especially the Pacific Coast is beyond doubt.

Geological resources of methanehydrates

Planetary, mainly aquatic development of gas hydrates, their poor, mostly fragmentary study, the extremely different scales of identified and forecasted (mainly by indirect signs) objects of their accumulation, have determined the wide range of estimates of their resources in the world - up to 10^{15}-10^{18} m^3. Almost all of them - 96-98% - fall on the bottom sediments of the World Ocean. There are more detailed information for some regions of the world. Thus, in the waters of the former Soviet Union (mainly in Russia) there are about $3.0 \cdot 10^{16}$ m^3 of gas hydrate (according to A.A. Trofimuk, N.V. Chersky etc.). In the Russian permafrost zone according to estimated of V.S. Yakushev in frozen accumulations the gas resources mainly in the unstable gas hydrates is estimated to $1.7 \cdot 10^{13}$ m^3. US Department of Energy of USA estimates its gas resources in gas hydrates to $5.7 \cdot 10^{15}$ m^3, while Gas Research Institute of the US – to $9.05 \cdot 10^{15}$ m^3 (2006), which are significantly more than the reserves of technically recoverable natural gas of the United States (according to the balance for 2009 – $6.9 \cdot 10^{15}$ m^3).

In Canada, according to conservative estimates, at a relatively detailed study of submarine gas hydrate potential, confirmed by core and well logging, total resources of methane in gas hydrates on the continental shelf and permafrost are estimated to $(0.44 - 8.1) \cdot 10^{14}$ m^3 [Axelrod, 2009] . This volume is located in (m^3):

Delta of Mackenzie River - Beaufort Sea -	$(0.24 - 8.7) \cdot 10^{13}$;
Arctic Archipelago -	$(0.19 - 6.2) \cdot 10^{14}$;
Atlantic outskirts -	$(1.9 - 7.8) \cdot 10^{13}$;
Pacific margin -	$(0.32 - 2.4) \cdot 10^{13}$.
Conventional gas reserves in 2011 –	$1.76 \cdot 10^{12}$ m^3.

In Japan, in the Nankai Trough the total resources of methane in gas hydrates is estimated at $6 \cdot 10^{13}$. Two objects were studied in more detail. First, in the range of depths of the sea 945 m, where in the depth of 207-265 m the accumulation of hydrate is forecasted, containing $1.21 \cdot 10^8$ m^3

of gas, and the second - at a depth of 0.8-1.0 km of the Sea of Japan, near the bottom, in 30 kilometers to the north from Dzotsu with resource $1 \cdot 10^{12}$ m^3. There are almost no conventional gas reserves on land in Japan, so the gas hydrates in Japan are considered as the real source of gas supply for 10 years, and in the future - for 100 years.

China in 2007 reported about reserves of gas in gas hydrates > $100 \cdot 10^9$ m^3 in the northern South China Sea. Conventional gas reserves in China in 2011 amounted to $3.04 \cdot 10^{12}$ m^3.

In India, the total volume of gas in gas hydrates as a whole is assessed mainly on indirect signs to $1.9 \cdot 10^{15}$ m^3, of which about $5.5 \cdot 10^{13}$ m^3 are identified in the Bay of Bengal at its eastern coast.

Conventional gas reserves in India for 2009 is $1.08 \cdot 10^{12}$ m^3.

It is possible that the region of the active outskirts of south-east Asia and Oceania, which developed in the Cenozoic stage of tectonogenesis, would be unique on a global on terms of accumulation of gas hydrates, but so far its study has just begun. In general, for the whole of this huge island-arc system at the junction of four planetary structures - the Pacific and the Indian thalassocratons ancient Australian platform and a thick array of south-east Asian continent is characterized by:

- extremely high seismic activity;
- a lot of active volcanoes (400), both on land and in the waters;
- frequent, essentially continuing earthquake, related to moves of lithospheric plates, including modern high-point (6-8 on the Richter scale);
- unevenly aged folds - from Baikalian to the Quaternary, with plenty of dislocations.

At the same time here, more than 12 petroleum basins are delineated within the limits of the continental shelf and on the islands, more than 250 mainly oil fields are opened and developed, including the giant field - Minos, but there is gas fields (Arun - 391 billion m^3). Mainly Cenozoic is productive, in depressions and through. There should be no doubts in the extensive development of intensive processes of gas hydrate formations in sediments and bottom sediments of the shelf, the basis is the warm sea rich in organic matter and therefore with active gas generation of methane from organic matter. The thermal stability of gas hydrates provides by ocean, waters of which are quickly align any excess of heat.

There is only unsolved question on the main source of gas, since here it can be anything - a biochemical benthic; catagenic from the depths of the movable and highly gas saturated cover.

Methodically, the majority of the above and other assessments of geological resources of gas hydrates (Q) is made on the same theoretical basis, as of resources of free gas, which is essential, given their genetic unity with the uniformity of the processes of organic matter transformation during diagenesis and the dependence of their phase state only on the thermodynamic environments in the environment of their location.

Calculations of Q hydrate were carried out by formula (1) by multiplying the area of hydrate-containing deposits, including areas of possible gas hydrate formation (S) on their thickness (h), porosity (n), the degree of capacitive filling of hydrate porosity (p) and the methane expansion coefficient - E during decomposition of gas hydrate, in order to transfer resources $Q^{g\text{-}h}$ into a volume equivalent of free phase:

$$\mathbf{Q} = \mathbf{S} \times \mathbf{h} \times \mathbf{n} \times \mathbf{p} \times \mathbf{E} \qquad (1)$$

The maximum value of E during full fill of cubic lattice of water molecules by methane is 164 m^3/m^3.

Obviously, none of these parameters can be adopted with at least a moderate degree of reliability in the present state of study of the problem. If you rely only on the areas with concentrated rather than dispersed volumes of gas hydrates confirmed by direct observations, than their submarine resources will not exceed 10^{14} - 10^{15} m^3 and will also be higher, because it is based on many assumptions. Global assessment of the geological resources of methane in gas hydrates are changed in the range of $2.5 \cdot 10^{16} – 7.6 \cdot 10^{18}$ m^3 [Ginsburg, Soloviev, 1995].

For comparison - the initial resources of conventional gas in the world is ~ $5 \cdot 10^{14}$ m^3, the current ~ $2.5 \cdot 10^{14}$.

We stress that we do not have a base to consider the mentioned above vast amounts of gas hydrates resources as an unconventional gas reserves in the short term. The main part of the bottom surface of the World Ocean (S) of 361 million km^2 belongs to the areas of possible gas hydrate formation, but only 20% of the area is covered by clastic sediments (sandy loam, siltstone, clay, etc.) with high biological productivity and consequently gas hydrate potential.

Deposits of alluvial fans from the continent of large rivers deposits (the Amazon, Ganges, etc.), with thickness up to 15 km and collapse arrays of shelf deposits at the foot of the continental slopes in areas with high seismic activity and dislocation of the sedimentary cover, providing not only the accumulation of biogenic methane but also the migration of the deep, catagenic methane with its transition to the solid phase when reaching areas of possible gas hydrate formation, are especially rich by organic matter, i. e. main gas generators. The basic parameters for the calculation of resources in gas hydrates - the area (S) - belongs to those territories. By multiplying it even on low quantities of other parameters in the formula (1), we obtain a priori the huge resources of gas hydrates, which are mentioned above and differs according to various estimates by 2-3 orders.

Approximately 26% of the ocean floor is covered by deep-sea pelagic clays. The rest of the surface of the ocean floor is occupied by mixed sediments - clastic, chemogenic, clay, silt, etc.

[Dyadin, Udachin, Bondaryuk, 1988] with low bio- and gas-productivity and absence of significant volumes of gas hydrates.

All these and many other data on the volume of gas in the gas hydrate accumulations of the world into its different areas, varying in the range of 2-3 orders, are given by the author to illustrate not only the huge amount of methane, conserved in the solid state, mainly in the aquatic environment of the bottom sediments of the World Ocean, but also poor level of its study as a whole, because it is necessary to assess their resources differentiated, primarily as geological and geochemical phenomena affecting a variety of planetary fluctuations and geotechnical characteristics of major and other properties of the soil, and also as a kind of gas feedstock, although in the long run. Since the purpose of this review is assessment of the resources of gas hydrates as an unconventional type of gas feedstock, than first of all, we need to determine, where and which gas hydrates accumulation are real for development in terms of condition, the economic indicators of production and the risks associated with the environmental impacts of their development. To do this, we need to continue their study and the most favourable extraction technology in the first.

Extraction of gas hydrates. Questions of industrial development of deposits of **gas hydrates** have been discussed for many years and there are different hypothetical models. There is no success yet, because there are no specific ideas about the kinds of accumulations of **gas hydrates**, which could be considered as a commercially important mineral deposits in terms of conditions of occurrence and reserves amount.

The gas hydrate production basis, taking into account their properties, may be represented by dissociation in situ, or extraction in solid state to the surface. The first experiments on the extraction of gas hydrates gas were undertaken jointly by several countries (USA, Canada, Japan, etc.) in the delta of Mackenzie River (Canada), and they are not yet completed. Modification of the stability conditions of gas hydrate, I. e. dissociation, can be obtained by the following: raising the temperature, pressure reduction, chemical inhibitors or complex effect. Despite the complexity of its implementation, especially in submarine conditions, technical reality of development of gas hydrates in the future is not excluded. Relatively detailed review of modern experimental methods of exploitation of gas hydrates based on foreign sources was produced in 2009 [Axelrod, 2009]. The review notes that researchers in recent years in the world focus on gas hydrate dissociation methods directly in situ.

The dissociation of gas hydrates by increasing the temperature in the hydrate-containing formation, or in the presence of free gas, its primary selection to reduce reservoir pressure and therefore a violation of the thermodynamic stability of gas hydrates, as well as an introduction of inhibitors to hydrate-containing formation (well), for example, $CaCl_2$ salt solutions, alcohol (methanol) and so forth is considered for the onshore accumulations of gas hydrates.

The use of the same methods of forced dissociation of gas hydrates in the marine environment is not only difficult, but hardly acceptable due to environmental consequences.

It is possible that the main obstacle for the extraction of gas hydrates in the water area will be not so much a technical-economic factors, but a negative environmental impact on marine bio resources, the nutritional value of which now and for the future is clearly exceed the practical importance of the production of gas hydrates for gas supplies.

Production of gas hydrates in the waters, where their basic resources and the largest accumulations (> 90%) are located, will repeat, but in the worst-case scenario for the environmental consequences, the experience of shale gas by hydraulic fracturing accompanied by the loss of land and sources of drinking water and service water supply in the regions of its development [Gornaya entsiklopediya..., 1987].

When choosing a gas hydrate development technology we must also be consider easily predictable potential danger of their production through the inevitable breakthrough of spontaneously forms gas bubbles to the surface. We recall that the explosion on the DH platform in the Gulf of Mexico has provoked rising of a gas bubble to the surface in the diesel compartment on the platform, which arose from the ascending gas flow in the gas-saturated oil leak from the well bottom with block leaking. The justification of this kind of accidents are always identical - "human factor" - not followed, failed to take timely preventive measures. However, in the case of breakthroughs of intense fluxes of methane bubbles to the surface, especially in a closed environment, we must not forget the obvious – the explosivity of the mixture of methane with air at its content of 5-16%.

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