MODERN FORMS OF DEVELOPMENT OF RESOURCE-SAVING TECHNOLOGIES FOR MINERALS MINING AND PROCESSING

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JUSTIFICATION OF THE CHOICE OF PNEUMATIC STRUCTURES FOR THE FORMATION OF GROUND STORAGE FACILITIES FOR THE GAS HYDRATES STORAGE

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Abstract

Natural gas can exist not only in gaseous, but also in liquefied and solid aggregate states. Natural gas in a solid state - gas hydrates of natural gas. It is in the solid state - in the form of gas hydrates - that natural gas can be stored in improved casing gas-resistant structures. In order to improve the pneumatic structures and the method of operation of these structures, the features of such storage are substantiated. The design and operation technology of the ground storage facility for the accumulation and storage of natural gas as part of the gas hydrate includes the main and some auxiliary elements. Compulsory components of a pneumatic structure include a fence, pumping equipment and a foundation. However, the main element of the ground pneumatic structure is a frameless gas-resistant shelter in the form of at least two dome-shaped gas-tight soft shells on a thermally insulated base. A necessary condition for the storage of gas hydrates of natural gas is the creation of thermobaric conditions higher than the dissociation parameters of gas hydrates of this composition. For increase the thermal resistance of the pneumatic coating, it is

suggested to fill the space between the shells with a porous substance with low thermal conductivity. Liquid compression foam is offered as a thermal insulation material. The use of liquid foams will increase the thermal resistance of soft shells and reduce the heat exchange between gas hydrates and the air outside. The use of these hydrate storages will significantly increase the efficiency and competitiveness of natural gas storage technology in the form of gas hydrates.

I. Introduction

As is known, at relatively low temperatures and a certain pressure, water molecules form a three-dimensional structure that can be occupied by gas molecules (for example, methane, ethane, carbon dioxide, etc.) [1]. This type of compounds are known as clathrates or inclusion compounds [2]. Today, a number of technologies are known in which gas hydrates are an intermediate or target product. These are the so-called gas hydrate technologies (transportation and storage of natural gas in gas hydrate form [1], gas hydrate fractionation, concentration using gas hydrates of any aqueous solutions [3, 4], etc.).

At the same time, the natural gas storage in gas hydrate form in many cases becomes a real alternative to traditional technologies.

Storage of gas hydrate requires maintenance of appropriate thermobaric conditions. However, gas hydrate can exist in a metastable state for some time as a result of the self-preservation effect or due to preservation by a ice layer of [4-6].

In addition, a compulsory condition for the reliable gas hydrate storage is the organization its high-quality thermal insulation and sealing. Such conditions should be ensured in specialized hydrate shelters. There are a number of projects, for example described in patent №US5964093, which involve the use of surface or partially buried capital structures built from traditional building materials.

However, warehouses made of traditional metal or reinforced concrete structures cannot provide effective sealing and thermal insulation. In fact, these structures can only perform the role of a skeleton for attaching insulating and sealing elements.

2. Theoretical substantiation

Taking into account the results of research on the development of parameters proposed in the work on the production of gas-hydrate blocks, the level of development of construction technologies and problems related to the provision of natural gas to consumers, an

analysis of the structures of potential storage facilities for the accumulation and long-term storage of blocks until the moment of consumption of dissociated gas was performed.

Light membrane structures best meet the specified storage parameters, among which pneumatic structures should be chosen (Fig. 1).

Membrane structures

Pneumatic structures   Pre-stressed structures

Air-supported structures   Pre-stressed membranes

Air-inflated structures   Hybrid systems
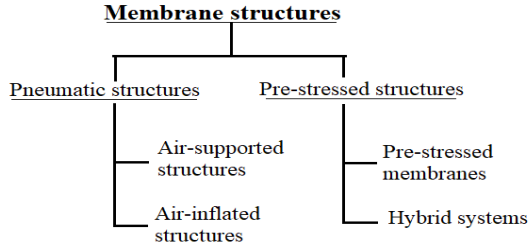
Fig. 1. Classification of membrane structures

A pneumatic structure is defined as a structure in which pressure drops of gas or air control and ensure shape stability [7]. Pneumatic structures are one of the most effective known structural forms. Constructions that use pressure as a stabilizing medium have been used for a long time, but they began to be used in the construction industry relatively recently [8].

Pneumatic structures are divided into two main types: air-controlled structures and air-stabilized structures. Among them, the construction with air stabilization is the most relevant for architectural applications [9].

Air-supported structures consist of only one membrane, which is supported by a small internal pressure difference. Thus, the internal air volume of the structure is under a pressure higher than atmospheric.

Air structures in which the enclosing membrane is supported by a small air pressure drop, such as stadium roofs, inflated storages. Pressure is created inside the entire structure. A low pressure is required to maintain a membrane-type structure; however, air leakage is very common because it is not possible to maintain a sealed structure. Therefore, membrane-type structures must have a constant supply of air to replenish the escaping air.

Air-inflated structures are supported by pressurized air contained

inside the inflated element of the building. The internal air volume of the building remains under atmospheric pressure.

Inflated structural elements are under high pressure and are used as structural elements in spatial construction. In this type of construction, high air pressure is maintained only inside the inflated members, which are the main load-bearing components of the structure.This system is more airtight than the membrane type, as it can be closed after inflation. The beam-type design is also more economical, as there is no need for constant air replenishment and less material is required.

The shape and stability of the air-stabilized structure is controlled by pressure differences across the membrane. In this type of pneumatic structures, there are several structures related to the number of membranes, types and magnitude of the pressure drop [8]. Therefore, in air-stabilized structures there are single-wall air structures and air-inflated structures (single wall air-supported structures and air-inflated structures) (Fig. 2).
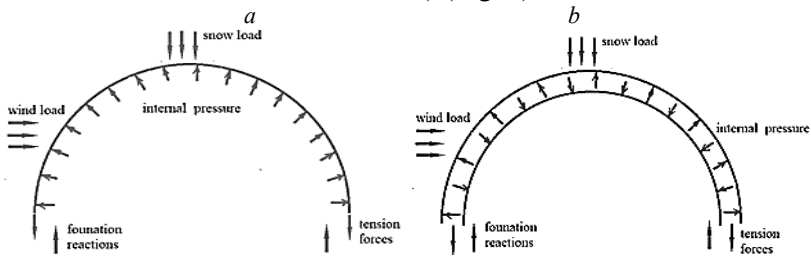
Fig. 2. Types of pneumatic structures: *a* - air support; *b* - air – inflated

Pneumatic designs are based on the theory of soap bubbles. A new roof construction technique, called pneumatic structures, is able to take a heavy load and withstand the effects of high-speed wind due to the pressure that holds the air inside the structure.

Forms created with soap bubbles are "ideal" pneumatic molds in which the membrane stresses are the same at every point on the surface. Such forms have the largest volumes and the smallest possible surface areas.

Obligatory components of pneumatic construction are enclosure, pumping equipment and foundation. Depending on the functional purpose, pneumatic structures also have other structural elements:

inlets, anchoring devices, power belts, fan and climate systems, reinforcing ropes, diaphragms, etc. [10]. Pumping equipment for an air-inflatable structure can be fans, blowers or compressors. First of all, pressure is created in the inner volume of the shell with the help of pumping equipment. This equipment is also used to maintain a stable pressure in the event of an air leak.

Structures are fixed to the ground with heavy anchors or attached to the foundation. Material weight and wind loads are used to determine the most suitable fastening system. For a small independent structure, ballast, concrete blocks or bricks can be placed around the perimeter of the sealing skirt to stabilize the structure. A larger and wider pneumatic structure requires reinforcing cables or nets to secure and stabilize it.

The main element of gas-resistant structures is a soft shell. There are many types of membranes used as roofs in pneumatic structures, including fabrics, hyperelastic materials (like rubber), composites, and more. The classification of membranes and tissues is shown in Fig. 3 [10].
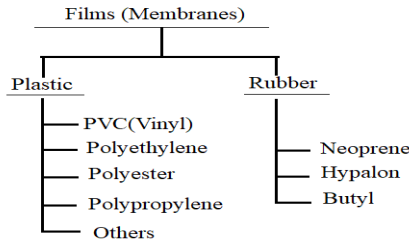
Fig.3. The classification of membranes and fabrics

It consists of the shell itself with a support contour and a number of technological components (fittings, non-return and ventilation valves, flanges, nodes for fastening power elements and equipment, etc.) [11]. However, the thermal performance of gas-resistant shells is low. Thin shells are not able to provide a sufficient level of thermal resistance. Therefore, to improve their thermal performance, it is advisable to cover these buildings with a two- and three-layer coating.

In addition, the amount of excess, relative to the environment, pressure in pneumatic two- and three-layer structures can be gradually changed from layer to layer, distributing the estimated total

excess pressure between the inflatable layers. This allows you to increase the load-bearing capacity and stability of the structure without increasing the strength of the structural material, while simultaneously maintaining increased tightness. At the same time, the inner shell is supported by the pressure difference between the room and the intershell space.

Modern technologies make it possible to obtain multi-layered and combined materials based on polymer films and synthetic high-strength fabrics. The main scheme of their design consists of three layers: a gas-tight film, a reinforcing base and a heat-welding layer. The two-layer gas-tight film is two orders of magnitude better than the performance of vulcanized rubbers. This is achieved by metallizing one or both sides of the film by vacuum spraying. However, the disadvantage of film materials is insufficient strength. Therefore, they are reinforced with fabrics [12].

In [13], it was indicated that the total coefficient of thermal conductivity of their two-layer shelters was 2.8-3.4 $W/(m^2 \cdot K)$, and when using internal reflective cladding it could be reduced to 1.7 $W/(m^2 \cdot K)$. Similar results can be obtained when using a suspension of a light shell, which forms a closed (isolated) air layer. Since the second dome is not structural, very light materials can be used for it. Even better insulating properties are achieved when an additional substrate (film) with a mirror coating is placed under the shell, for effective reflection of thermal radiation.

Thanks to the air layer, the overall coefficient of thermal conductivity decreases and thus heat loss decreases.

Single-layer or double-layer membranes can be made of industrial fabrics such as fiberglass or polyester, which provides great stability. The shell shape is a very important aspect in pneumatic designs. If the pressure on the pneumatic structure is uneven, the membrane creates wrinkles and stress points, which will lead to its destruction. However, the membrane (covering) of structures with such fabrics is quite unreasonably expensive.

Therefore, the most widely used material for air-resistant structures is a fabric made of nylon or polyester fibers covered with plasticized polyvinyl chloride (PVC) or chlorosulfonated polyethylene (hypalon) [13, 14]. The service life when using ordinary materials is usually 7-10 years. However, with high-quality

operation, pneumatic structures have been in continuous operation for more than 15 years, at the same time withstanding stormy winds without damage [13]. Fluorine-containing polymers are successfully used to create more durable materials.

Based on the features of gas storage in gas-hydrate form, it is suggested to use a two-layer coating with a barrier layer of non-flammable gas or gas mixture for gas-resistant hydrate storages. Also, in order to limit the supply of energy from the soil to the storage, it is necessary to provide thermal insulation of its base.

In addition, information on the composition of the non-flammable gas mixture injected between the layers of the coating, divided into separate isolated sectors, is proposed to be used to control their integrity. The nature of the change in the composition of the gas will indicate a violation of the tightness of the outer or inner shell, respectively.

In gas-resistant structures, which are proposed to be used as hydrate storage, it is necessary to maintain a temperature regime that allows the gas hydrate to be in a stable state at a pressure close to atmospheric. It is proposed to ensure the necessary temperature regime of the storage for the cold and warm periods of the year due to the accumulated cold in the gas-hydrate blocks and the additional cooling system.

Effective thermal insulation can be provided by a relatively thin layer of porous material (foam, mineral wool, etc.), and high-quality sealing by a polymer film [10, 12, 13].

Based on this, it is proposed to use gas-resistant pneumatic structures as hydrate storages [10, 14]. At the same time, modern coatings allow maintaining their operational characteristics for a long time (up to 15-20 years) [10]. In addition, they can be easily dismantled, transported and quickly assembled, that is, they can be considered as mobile technological objects.

These buildings are structures supported by a gas cushion. However, the pressure in them is higher than atmospheric only to ensure the force for the formation of a dome-shaped form and to compensate for the mass of the shell itself (in the range of pressure – 0.01-1.0 MPa) [9].

However, the thermal resistance of such structures is insignificant [15]. Therefore, they need their conditioning (cooling). Taking into

account the costs of cold production, it is impractical to operate such buildings without the organization of additional thermal insulation.

A variant of increasing the thermal resistance of these structures is the use of two- and three-layer coatings. However, the thermal resistance of the barrier gas layer increases noticeably only up to its thickness of 0.3 m [16, 17]. For example, the coefficient of thermal conductivity of the two-layer shelters considered in [18] was 2.8-3.4 W/(m^2·K). Therefore, regardless of the external temperature, a significant heat flow will enter the storage even through a double-layer coating.

Taking into account the results of research on the development of the parameters of the gas hydrate blocks proposed in the work, the level of development of construction technologies, and problems related to the provision of natural gas to consumers, it is proposed to accumulate and store it for a long time until the moment of consumption in ground hydrate storage facilities in the form of gas-resistant structures covered with soft shell These structures are closed structures that "lie" on an air (gas) cushion, the pressure in which is excessive, but exceeds the atmospheric pressure only to overcome the effort of forming (bending) and compensating the shell's own weight. They are operational in the region of the so-called Laplacian overpressure (0.01-1.0 MPa), which belongs to the low level [14]. The use of this type of surface hydrate storage can significantly smooth out the seasonal unevenness in gas production and in some cases be a serious alternative to underground gas storage.

2.1. Improvement of the storage thermal insulation system

It is known that the thermal insulation properties of materials are determined by their porosity. The pores are filled with gas of low thermal conductivity. As thermal insulation, among others, materials are used, which are polymers, foamed before the start of hardening. Hardening, in this case, is required for the production of heat-insulating panels of a certain shape and size for the convenience of their use and transportation.

However, the phase state of material bubbles does not affect its thermal insulation properties. Therefore, the use of solid porous thermal insulation materials is due to the convenience of their use. In the case of gas-resistant shell structures, the use of solid heat-

insulating materials will be unacceptable, as this will significantly complicate the construction and duration of the shelter installation.

Therefore, it is proposed to use liquid polymer foams as a material for thermal insulation of gas-resistant shell structures - storage of gas hydrates. At the same time, in the case of using a transparent shell-shelter, the foam will allow part of the scattered sunlight into the storage. This will make it possible to regulate the supply of energy to the storage to some extent.

Foams are coarsely dispersed highly concentrated systems in which the dispersed phase is gas bubbles, and the dispersion medium is liquid in the form of thin films. The concentration of gas bubbles should be more than 74% (by volume). Foams are thermodynamically unstable systems.

In foams, gas bubbles are pressed against each other by a thin layer of dispersion medium - foam films. The system is in stable equilibrium when contact is made between three bubbles. Liquid films between these bubbles form a Plateau triangle, and the contact points of the films and their thickening are Plateau-Gibbs channels (Fig. 4).

Fig.4. Cross-section of the Plateau channel: *1* – liquid films; *2* – Plateau-Gibbs channel

The main characteristics of foams are: multiplicity, dispersibility, stability over time. The ratio of the volume of the formed foam to the volume of the dispersion medium characterizes the multiplicity of the foam. The multiplicity of the foam increases with the increase in the size of the gas bubbles (cells) and the thinning of their walls.

The dispersion of the foam is estimated by the size (radii) of the bubbles. Usually, real foam is polydisperse and gas bubbles in it are of different sizes. Polydispersity of foams affects its stability over time [19].

The stability (stability) of the foam is its ability to maintain the total volume, dispersion and prevent the outflow of liquid (syneresis). The stability of the foam increases as the cell size decreases and the thickness and strength of the polymer film that

forms the cell increases.

Foam stability is divided into two types:

- kinetic (sedimentation) stability – the ability of the system to keep the distribution of particles of the dispersed phase unchanged over time in the volume of the entire dispersed system, the ability of the system to resist the force of gravity;

- aggregative stability - the ability to keep the size of particles of the dispersed phase unchanged (maintain dispersity).

Violation of the sedimentation resistance of the foam is caused by the action of gravity and capillary suction forces. There is a process of spontaneous swelling of the liquid in the foam film, its thinning and rupture. The movement of fluid against gravity is explained by capillary effects due to the fluid pressure gradient in the Plateau channels.

Aggregative stability of the foam is formed by the mono- or polydispersity of gas bubbles and occurs under the influence of gas diffusion. The smaller the gas bubble, the greater the pressure in it. Over time, there is a process of gas diffusion from small bubbles to large ones, while the small bubbles decrease in size and the large ones increase in size. This leads to a change in the stability of the foam, the foam "ages" and breaks down. The destruction of the foam structure (change in its dispersed composition) occurs as a result of the diffusion transfer of gas between the foam bubbles and the destruction of the bubble films, which leads to their fusion (coalescence). A higher degree of polydispersity causes a significant manifestation of gas diffusion, although this process is quite slow.

Foams are typical lyophobic systems. Thermodynamically, they are not stable due to the diffusional transfer of gas and the swelling of the dispersion medium under the influence of gravity, which lead to a change in the structure and gradual destruction of the foam.

It is known that the size of the foam bubbles and their homogeneity [20] depend on the type and concentration of the foaming agent, the presence of a stabilizing substance, the ratio of the consumption of the aqueous solution of the foaming agent and air, and the methods of their formation. One of the most promising in terms of aggregate resistance is compressed air foam - a homogeneous, fine-structured foam of low multiplicity, obtained by mixing a foaming agent, water and compressed air or nitrogen. The

stability of the compression foam increases when the diameter of the bubble decreases [21].

The main components of foaming agents are surfactants (surfactants). Colloidal surfactants or high molecular structures (HMS) are usually used as a foaming agent. Usually, middle members of homologous series are used as foaming agents, and anionic surfactants are better than cationic and neonogenic surfactants. Polyelectrolytes, such as proteins, are the best foaming agents among high molecular structures (HMS).

An important role is played by the concentration of the foaming agent. For foaming agents - colloidal surfactants, the maximum foaming capacity is reached in a certain interval of concentrations, and with its further growth, it remains constant or even decreases. In the case of HMS, the foaming ability increases with increasing concentration.

A change in the properties of the foam is possible when stabilizers are added to surfactant solutions. Their action is based on increasing the viscosity of solutions and slowing down the flow of liquid due to this, i.e., a structural-mechanical factor is added to the action of the kinetic stability factor characteristic of foaming agents - surfactants. For example, substances that increase the viscosity of the foaming solution itself (thickeners) can be used as such stabilizers for surfactants or HMS for thermal insulation of gas-resistant shell structures. They are added in large concentrations. These are glycerin, ethylene glycol, methyl cellulose. Cellulose derivatives already in the amount of 1-2% increase the viscosity of the solution and the stability of the foam tenfold, which leads to a strong slowdown in the process of dehydration of films. Colloidal stabilizers are more effective than thickeners. These include: gelatin, glue, starch, agar-agar. These substances, taken in the amount of 0.2-0.3% of the mass of surfactant, increase the viscosity of the liquid in the films by more than 100 times, and the stability of the foam increases by 2-8 times.

In addition, substances that polymerize in the volume of the foam can be used. Polymerization significantly increases the strength of films, but their transition to a solid state is possible. These are the most effective stabilizers. These can be polymer compositions - synthetic resins, for example, urea or latex.

Stabilizers can be substances that participate in the construction

of adsorption layers at the boundary of the "liquid-gas" separation. The main representatives are fatty alcohols, mainly tetradecyl alcohol. The introduction of only 0.05% alcohol into solutions of foaming agents greatly reduces the surface tension, which leads to an increase in the stability of foams

Mineralized (three-phase) foams can also be used [20, 21]. They are obtained when finely ground solids are added to the foam to increase its strength - talc, asbestos, quartz, carbon black, which, when evenly distributed on the surface of the bubbles, strengthen the films and extend the life of the foam. The strengthening of the foam occurs due to the adhesion of solid mineral particles to the foam bubbles, due to the interaction between the surface of the solid particle and the polar groups of the surfactant. Fine powders give strong foam films. The stabilization mechanism of three-phase foams (gas-liquid-solid particles) is primarily explained by the narrowing of the Plateau channels. As a result of decreasing the diameter of the channel, the rate of outflow of the solution decreases and corks made of grains that did not stick to the bubbles additionally clog these channels.

Taking into account the above, for the thermal insulation of gas-resistant shell structures, surfactants or HMS can be used together with any of the named stabilizers or three-phase foams.

The schematic diagram of such a storage-shelter, supplemented by a complex of appropriate equipment for the implementation of the technological process of gas hydrate storage and regasification, is presented in Fig. 5.

Its main elements are shelter, base and auxiliary equipment. The shelter of the hydrate storage-shelter consists of a liquid foam layer between several impermeable to gas and water canvases 2 and 4 with a sun-reflective layer on top.The shelter is fixed by a net made of ropes 5. The storage-shelter is equipped with the following systems: foam generation and selection of products its destruction; storage conditioning (cooling and heating); gas and water selection.The foam generation system involves supplying the produced foam to the upper part of the space between the inner and outer shells. At the same time, a system for selecting of foam destruction products is placed between the shells at the base level.
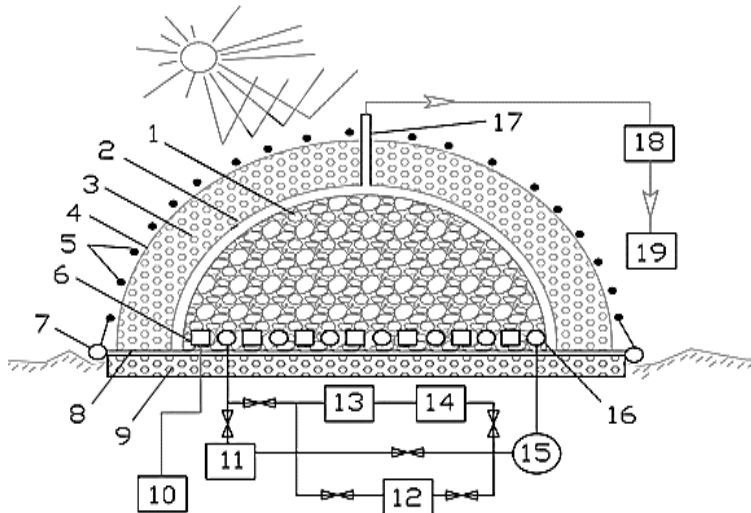
Fig 5. Schematic diagram of hydrate storage-shelter at the gas hydrate storage stage: 1 – gas hydrate; 2 – the lower fabric for the shelter; 3 – a liquid foam layer; 4 – the upper fabric for the shelter; 5 – a system of external reinforcement of the shelter in the form of a net made of ropes; 6 – perforated pipes of the gas and water extraction system from under the gas hydrate stack; 7 – a hermetic connection system of the cover sheets and the base; 8 – base covering made of material impermeable to gas and water; 9 – heat-insulating coating of the base; 10 – water collection tank; 11 – system of heating the coolant based on the solar collector; 12 – coolant heating block; 13 – unit of the refrigerating unit; 14 – air cooling system; 15 – circulation pump; 16 – heat exchanger pipe system; 17 – gas selection system; 18 – gas compression unit; 19 – gas consumer [9]

For the maximum energy efficiency of the technology, the level of gas hydrate cooling in the production process is determined, taking into account the duration and parameters of transportation and storage.

The flow of thermal energy from the ground through the base of the storage at its average value of 17 W/m² [22] will be 0.03 MW. Thermal insulation of the base will allow to reduce it to 9 kW. After the preparation of the site, the base of the storage-shelter is arranged by sequentially laying a layer of thermal insulation 9 (Fig. 5), a coating of water- and gas-tight material 8, a heat exchanger in the form of a system of pipes 16, a system of gutters and perforated pipes 6 for the removal of gas and water.

For reliable sealing of the hydrate storage-shelter, system 7 seals the connection between the shelter sheets and the base. The isolated space formed is connected to the compressor 18 by the gas discharge line 17. The temperature regime of the hydrate storage is ensured by the accumulated cold in the gas hydrate and the additional air conditioning system. Hydrate dissociation is proposed to be carried out directly in the storage at the expense of solar energy. The temperature of the gas hydrate (cooling during storage and heating in the process of gas extraction) is maintained by pumping the cooled or heated coolant through the heat exchanger 16 at the base of the hydrate storage-shelter.

The coolant is cooled by a refrigerating unit 13 or an air cooling system 14. Cooling or heating of the coolant is carried out in the solar collector 11, heater 12, refrigerating unit 13, air cooling system 14. Gas selection is carried out as a result of controlled dissociation of gas hydrate when pumping the coolant through the heat exchanger 16. Water is discharged from the storage-shelter to the tank 10 by the collector 6. (In addition, it is possible to organize the inflow of solar energy through the transparent areas of the shelter).

Gas through the selection line 17 enters the compression unit 18. Then it is consumed by the gas distribution network. The pressure in the line is limited by the mechanical strength of the shelter and lies within 0.2-0.4 MPa. The mobility of the storage-shelter will allow them to be placed directly near the objects of consumption. This will allow the gas during pressure dissociation to be sent to the gas distribution network without additional compression.

3. Calculation of storage-shelter operational parameters

The thermal resistance of the coating, which characterizes the heat-shielding characteristics of the gas-resistant storage-shelter, is determined by the formula

$$R_{stor} = \frac{1}{\alpha_1} + \frac{2\delta_{shel}}{\lambda_{shel}} + R_{barr} + \frac{1}{\alpha_2}, \tag{1}$$

where R_{stor} - reduced thermal resistance of the storage-shelter shell, $m^2 \cdot K/W$; α_1 i α_2 - coefficients of heat transfer of external and internal air, respectively $W/m^2 \cdot K$; δ_{shel} - thickness of the gas-tight shell fabric, m; R_{barr} - thermal resistance of the barrier layer, $m^2 \cdot K/W$; λ_{shel} - coefficient of thermal conductivity of the shell fabric, $W/m \cdot K$.

The average temperature for the forest-steppe zone of Ukraine for January is 265 K, July - 293 K [14, 15]. The thermal resistance of the storage-shelter cover (R_{stor}) in summer will be 0.27 m$^2 \cdot K/W$, in winter - 0.35 m$^2 \cdot K/W$. Then, during the winter period, energy will flow into the storage-shelter

$$q_W = \frac{1}{R_{stor}}\left(t_{out} - t_{in\,stor}\right)\left(\frac{W}{m^2}\right) \qquad (2)$$

where t_{out} i $t_{in\,stor}$ - air temperature, respectively, outside and in the storage-shelter, K.

$$q_W = \frac{1}{0,35}\left(265 - 248\right) = 48,6 \ (W/m^2).$$

The heat flow in the hydrate storage in the summer (q_s) will be [16]

$$q_s = q_{av.d} + k \cdot A_d = 1 / R_{stor.s}(((t_s + p_{rad} \cdot I_{rad} / \alpha_{surf}) - t_{in\,stor}) +$$
$$+ k \cdot (0.5 \cdot A \cdot K_m + prad\,(I_m - I_{rad}) / \alpha_{surf})), \qquad (3)$$
$$q_s = 105.0 \ (W/m^2),$$

where A_d - daily fluctuation of heat energy flow, W/m^2; $q_{av.d}$ - average daily heat energy input to the storage, W/m^2; k - daily coefficient of change of heat flow A_d; t_s, $t_{in\,stor}$ - the temperature of the outside air in July and inside the storage, respectively, K; p_{rad} - coefficient of absorption of heat of solar radiation by the external surface of the storage; I_{rad} - average daily amount of solar radiation reaching the storage surface in the warmest month, MJ/m^2; α_{surf} - coefficient of heat absorption of the external surface of the storage for the warm period of the year; K_m - the maximum amplitude of daily air temperature fluctuations in the warmest month of the year, $^\circ K$; I_m, $I_{av.d}$ - maximum and average daily value of the amount of solar radiation, respectively, MJ/m^2.

The results of calculations of thermodynamic parameters for gas hydrate storage in a storage-shelter with a two-layer coating and an air barrier layer are given in table. 1.

Gas hydrate storage parameters in a double-layered storage with an air barrier layer

Thermodynamic parameters	Calculations for the average monthly temperature	
	winter	summer
Thermal resistance of the storage-shelter shell, R_{stor}, m^2·K/W	0.35	0.27
Heat flow to gas hydrate without thermal insulation layer, q, W/m^2	48.6	105.0

Taking into account the thermal resistance, the thermal inertia of the two-layer cover of the hydrate reservoir will be [11]

$$D_{ther.in} - 0.27 \cdot R_{stor}\sqrt{\lambda\rho c} \qquad (4)$$

where $D_{ther.in}$ - thermal inertia; R_{stor} - thermal resistance, m^2·K/W.

$$D_{ther.in} - 0.27 \cdot 0.27 \div \sqrt{0.0244 \cdot 1.29 \div 717} = 0.4 \, D_{ther.in} < 1.5$$

Therefore, such a coating is inertialess. Let's consider the option of reducing the heat flow through a two-layer coating when filling the space between them with stable foam (foam density 4.0 kg/m^3, layer thickness (δ_{coat1}) - 1.5 m, coefficient of thermal conductivity (λ_{coat1}) - 0.041 W/(m·K)) using an example storage with a capacity of 3,000 tons of gas hydrate (5.4 million cubic meters of natural gas).

The coefficient of thermal conductivity λ_{coat1} of a two-layer reinforced coating with a thickness of 2 mm is 0.16 W/m·K [17]. Then its thermal resistance R_{coat1} will be at the level of 0.0125 m^2·K/W. The thermal balance of the storage-shelter is described by the equation

$$Q_1 + Q_2 - Q_3 - Q_{add} = 0, \qquad (5)$$

where Q_1 - heat flow into the storage through the shell, J; Q_2 - heat flow from the base of the storage, J; Q_3 - cold accumulated by gas hydrate, J, Q_{add} - additional heat removal (cooling), J.

The reduced thermal resistance of the coating is determined by the formula

$$R_{stor\,coat} = \frac{1}{\alpha_{out}} + \frac{2\delta_{coat1}}{\lambda_{coat1}} + \frac{\delta_{coat2}}{\lambda_{coat2}} \ ,$$

where $R_{stor.coat}$ - redused thermal resistance of the storage-shelter coating, m^2·K/W; α_{out} - coefficient of heat transfer of outside air,

Вт/(м²·K); δ_{coat1} - coating layer thickness, m; λ_{coat1}- thermal conductivity coefficient coating, W/m·K; δ_{coat2} - thickness of the foam layer, m; λ_{coat2} - coefficient of thermal conductivity of the foam layer, W/m·K.

Therefore, the reduced thermal resistance of the storage-shelter cover ($R_{stor.coat1}$ and $R_{stor.coat2}$) for winter and summer will be 37.78 and 37.62 m²·K/W, respectively. Then, in winter, the heat flow into the storage from the outside will be

$$q_{W1} = \frac{1}{R_{stor\cdot coat1}}\left(t_{out} - t_{in.rtor}\right)\left(W/m^2\right) \tag{7}$$

where t_{out} and $t_{in\ stor}$ - air temperature, respectively, outside and in the storage, K.

$$q_{W1} = \frac{1}{37,78}\left(265 - 248\right) = 0{,}45\left(W/m^2\right)$$

The total heat flow into the storage-shelter through the coating Q_{w1} in the winter period will be 1.76 kW.

The heat flow to the storage in the summer (q_{s1}) was determined by the formula

$$q_{s1} = 1/R_{stor.coat2}(((t_{out} + p_{rad}\cdot I_{rad}/\alpha_{surf}) - t_{in\ stor}) +$$
$$+ k\ (0{.}5\cdot A\cdot K_m + p\text{rad}\ (I_m - I_{rad})\ /\alpha_{surf})), \tag{8}$$
$$q_{s1} = 1{.}33\ \ W/m^2.$$

The total heat flow into the storage through the coating (Q_{s1}) in the summer period will be 5.23 kW.

The heat flow that enters the gas hydrate from the base (Q_2), with its average annual value for mid-latitudes of 0.17 W/m² [15], will be 0.3 kW. Its insulation will reduce heat input to 0.25 kW.

In the table 2 shows a comparison of the calculated parameters of gas hydrate storage in ground-based gas-resistant storages in variants of the air layer between shells and foam.

Therefore, the required capacity of the additional cooling system of the storage-shelter for storage of gas hydrate without its dissociation (at a temperature of 258 K) is 0.9 kW in the winter period, and 4.44 kW in the summer period.

Table 2

Comparison of gas hydrate storage parameters in ground gas-resistant storage-shelters depending on the level of thermal insulation

Thermodynamic parameters	Calculations for the average monthly temperatureи	
	winter	winter
Thermal resistances, $R_{stor.coat,}$ m^2 ·K/W:		
- air between the fabrics of the shell	0.27	0.35
- a layer of foam between the fabrics of the shell	37.78	37.62
Heat flow to storage-shelter, q, W/m^2:		
- air between the fabrics of the shell	48.6	105.0
- a layer of foam between the fabrics of the shell	0.45	1.33
Heat flow to storage-shelter, $Q_{1,}$ kW:		
- air between the fabrics of the shell	189	408.0
a layer of foam between the fabrics of the shell	1.76	5.23
Energy costs for cooling, Q_3, kW:		
- air between the fabrics of the shell	190.2	409.2
-a layer of foam between the fabrics of the shell	2.1	5.5

4. Modeling of heat exchange processes

Let's set the temperature on the surface of the gas hydrate as a result of the arrival of heat flow, as a process of heat transfer through a multilayer coating. On one side of the coating is the external environment with a temperature of T_p, and on the other – cooled to a temperature of T_g. gas hydrate (Fig. 6).
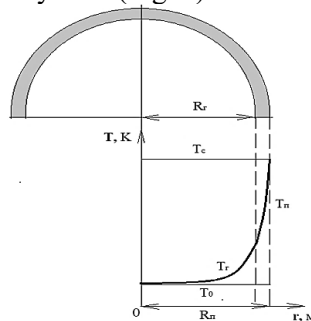

Fig. 6. Scheme of the gas hydrate heating process in the storage-shelter

Formulation of the problem. Let's assume: the initial temperature of the gas hydrate (T_0) is 248 K; the gas hydrate stack has the shape

of a hemisphere with a base radius (R_g) of 23.5 m; the surface of the gas hydrate is covered with a 1.5 m layer of foam (R_s–R_g=1.5 m); the initial temperature of the foam is 248 K; there is thermal contact between the foam and the hydrate; the temperature of the outer surface of the storage-shelter (T_{out}) is constant and is 293 and 265 K for summer and winter, respectively.

It is necessary to find the temperature distribution over time and establish the moment when the temperature of the surface of the gas hydrate reaches 258 K (equilibrium temperature).

This process is described by a system of differential equations.

The change in gas hydrate temperature is described by the equation

$$\frac{\partial[rT_g(r,\tau)]}{\partial\tau} = a_g\frac{\partial^2[r,T_g(r,\tau)]}{\partial r^2}(\tau>0,\ 0<r<R_g); \qquad (9)$$

Temperature change in the foam layer as a result of heat exchange with the gas hydrate and the external environment

$$\frac{\partial[rT_g(r,\tau)]}{\partial\tau} = a_g\frac{\partial^2[r,T_g(r,\tau)]}{\partial r^2}\ (\tau>0,\ R_g<r<R_s); \qquad (10)$$

$$\frac{\partial[rT_\downarrow(r,\tau)]}{\partial t} + \alpha(T_{out}-T(R,\tau)=0\ T_{out}\text{-}\ T(R,\tau))=0; \qquad (11)$$

Initial conditions of the process
$$T_g(r,0)=T_o;\quad T_s(r,0)=T_o; \qquad (12)$$

Boundary conditions of the process

$$T_g(R_g,\tau)=T_s(R_g,\tau);\ \ \lambda_g\frac{\partial T_g(R_g,\tau)}{\partial\tau}=\lambda\frac{\partial T_s(R_g\tau)}{\partial\tau}$$

$$T_s(R_s,\tau)=T_{out};\ T_s(R_s,\tau)=T_{out};\ T_g(0,\tau)\neq\infty \qquad (13)$$

where r - variable (current) value of the radius of the storage base, m; R_g - radius of the base of the storage-shelter located under the gas hydrate embankment, m; R_s - the radius of the base of the storage-shelter, which is located under the gas hydrate mound and the foam layer, m; T_o - storage temperature of gas hydrate, initial temperature of gas hydrate and foam layer, (T_o=248), K; T_{out} ambient temperature (293 K in summer, 255 K in winter); T_g variable over time (current) gas hydrate temperature, K; T_s - variable over time (current) temperature of the foam layer, K; τ - the time of the heating (cooling)

process of gas hydrate and foam; λ_g - coefficient of thermal conductivity of gas hydrate, W/(m K); λ_s - coefficient of thermal conductivity of foam, W/(m K); a_g - coefficient of thermal conductivity of gas hydrate, m²/s; α - heat transfer coefficient, W/(m² K); a_s - coefficient of gas hydrate thermal conductivity, m²/s.

In order to evaluate the thermal insulation characteristics of the foam and the dynamics of the temperature change of the gas hydrate in the gas-resistant storage-shelter, its computer simulation was carried out (Fig. 7-10). The above storage calculation parameters were taken as the starting point.
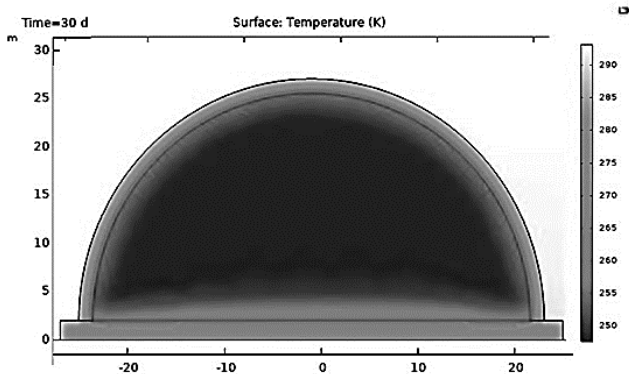

Fi. 7. Simulation of heat exchange in summer (external temperature 293 K) of gas-resistant hydrate storage-shelter thermally insulated with liquid foam without additional cooling after 30 days of storage
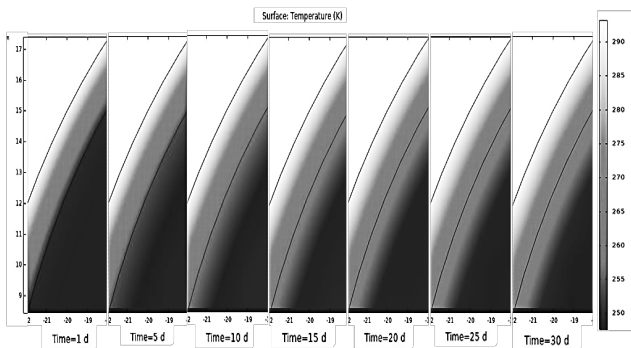

Fig. 8. Dynamics of changes in the temperature of the gas hydrate surface and the foam layer in the hydrate storage-shelter in the summer (*T*= 293 K) without additional cooling
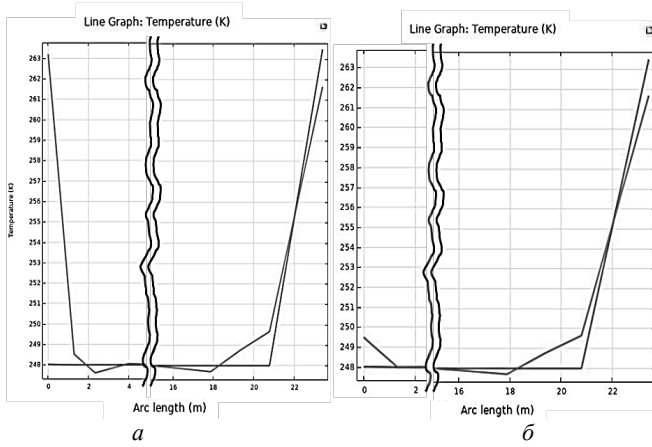
Fig. 9. Dynamics of changes in the temperature of the gas hydrate (with an initial temperature of 248 K) from the surface to the center of the sole of the stack in the summer period of storage (*T*= 293 K) without additional cooling, provided that it is thermally insulated with a layer of foam 1.5 m thick: a) at the end of the first days of storage; b) at the end of the thirtieth day of storage
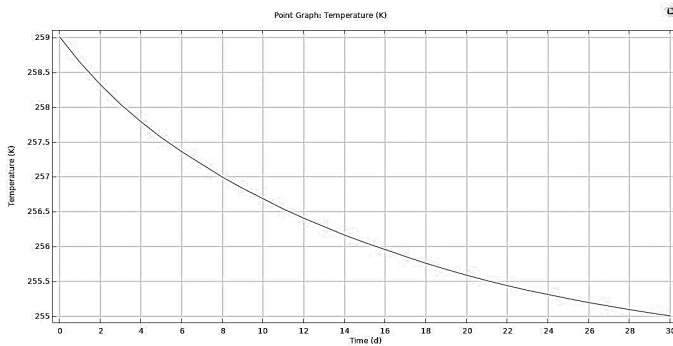

Fig. 10. Dynamics of changes in the temperature of the gas hydrate surface (with an initial temperature of 248 K) during thirty days in the summer storage period (*T* = 293 K) without additional cooling, provided that it is thermally insulated with a layer of foam 1.5 m thick

Therefore, with an initial temperature of gas hydrates of 248 *K*, its additional cooling when stored in a storage-shelter facility insulated with foam, even in the summer months, will be necessary after 30 days of storage (to maintain the temperature of the gas hydrate at a level not higher than 258 *K*).

In winter, at an average air temperature of 265 *K*, storage of gas hydrate is possible without additional cooling.

At the same time, under the condition of gradual selection of gas, which will be released from the surface of the gas hydrate layer, the storage-shelter can be operated without cooling during the entire storage cycle.

Conclusions

Thus, gas storage in gas hydrate form is proposed to be implemented in improved shell gas-bearing structures.

This improvement consists in the use of liquid stable foams as a thermal insulation material.

The main design elements of this storage-shelter facility are a frameless gas-resistant shelter in the form of at least two dome-shaped gas-tight soft shells on a thermally insulated base, the space between which is filled with liquid foam.

The use of these hydrate storages will significantly increase the efficiency and competitiveness of natural gas storage technology in the form of gas hydrates.

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