Досліджено технологічну та екологічну ефективність видобування метану з природних морських покладів гідратів за допомогою різних методів. Встановлено, що одним із найефективніших способів екологічного видобування метану з морських газогідратних покладів може стати метод заміщення. Визначено можливість використання різних гідратоутворюючих газів у якості газів заміщення, а також доведено найбільшу екологічну ефективність сірководню

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Ключові слова: газогідратні поклади, морські гідрати, видобування метану, сірководень, утилізація діоксиду вуглецю

Исследована технологическая и экологическая эффективность добычи метана из природных морских залежей гидратов с помощью различных методов. Установлено, что одним из наиболее эффективных способов экологической добычи метана из морских газогидратных залежей может стать метод замещения. Определена возможность использования различных гидратообразующих газов в качестве газов замещения, а также доказана наибольшая экологическая эффективность сероводорода

Ключевые слова: газогидратные залежи, морские гидраты, добыча метана, сероводород, утилизация углекислого газа

1. Introduction

The issue of gas hydrates, both industrial and natural, has been the object of thousands of studies by highly skilled professionals in many countries [1-9]. Extraction of organic gases such as methane, ethane, propane and butane, from marine gas hydrate deposits is of great interest in the world, but it can have unwanted consequences. Submarine hydrates are the physical and geological phenomenon that occurs in all oceans and many seas of the world, and it is associated with the peculiarities of the seabed, the bottom layers of sedimentary rocks, and the thermal field of the ocean floor.

The process during which natural gas hydrates are formed is divided into two stages: a primary one, which refers to the formation of gas hydrates from water and natural gas, and a secondary one, which coincides with gas migration and deposit reformation through multiple changing temperature conditions in the geological history of the Earth [1]. It is not clear, however, what geological and physical properties are contained in these clusters, how they are formed, or how they are distributed. It is known [2] that there are four conditions of synthesis of gas hydrates: sufficient concentration of gas, sufficient concentration of water, a relatively low temperature, and a rather high pressure. However, the conditions of their destruction and renewal have been insufficiently studied. UDC 662.767.1

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A METHOD DEVELOPED TO INCREASE TECHNOLOGICAL AND ECOLOGICAL EFFICIENCY OF GAS PRODUCTION FROM HYDRATE DEPOSITS

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The total reserves of gas hydrates in the world, by quite pessimistic estimates, exceed the known reserves of conventional gas of 187.1 trillion m³ (according to the data of the BP Statistical Review) [3], and the tentative estimates amount to at least 250 trillion m³. About 98 % of world reserves of gas hydrates are concentrated in the ocean, whereas 2 % – on land in permafrost. Theoretical studies by Ukrainian scientists [4] confirm the feasibility of comprehensive research because, by preliminary estimates, in the Ukrainian economic zone of the Black Sea methane reserves are equal to at least the 100-year volume of natural gas extraction in Ukraine. So, if methane from the sea is extracted as intensely as it is mined on land, it will still last for 1,000–1,500 years.

However, it should be noted that there may be serious environmental problems in the development of gas hydrate deposits and in the changes of thermodynamic conditions close to the limit of the gas hydrate stability phase. Therefore, the development of the Black Sea gas hydrates can ensure energy independence of Ukraine only in the case of an effective and environmentally safe method of gas extraction.

The relevance of this study is based on the fact that through researching the conditions of hydrate formation and destruction of hydrates it is necessary to determine the possibility of controlling the processes of hydrates destruction while extracting gas by replacing methane with another generated gas hydrate.

2. Analysis of previous studies and statement of the problem

In September 2009, deposits of gas hydrates were found in the East China Sea [5] and in the mountains of Tibet. China is interested in developing these deposits on the basis of scientific justification of new methods of extracting gas from gas hydrate deposits. According to many experts, the methods of gas extraction from gas hydrate deposits should be based on a physical impact [6], namely on reducing pressure or increasing temperature, regardless of the difference between the deposits being marine or terrestrial.

The Japan Oil, Gas and Metals National Corporation, also known as JOGMEC, is a Japanese government independent administrative institution that for the first time in the world managed to extract gas from methane hydrate on the ocean floor [7]. A trial batch of natural gas was extracted from a depth of 1.3 kilometres of the Pacific Ocean deposits of methane hydrate at a site located in the south of the main Japanese island of Honshu. Experts have preliminarily estimated the proven reserves at the volume of natural gas in Japan for 14 years [8]. In 2012, a Japanese research vessel Tikyu leased by the Japan Oil, Gas and Metals National Corporation started test drilling under the ocean bottom, 70 kilometres south of Atsumi Peninsula (near Nagova) to experiment with extraction of methane hydrates. Drilling of three wells was conducted at the depth of 260 m (whereas the depth of the ocean in this place is about a kilometre) to test whether extraction of gas hydrates was possible and to take measurements. To convert methane hydrates into gas, the process used was decompression (pressure reduction), developed by a consortium of MH21. The trial operation of this field has revealed interesting features of the development of marine gas hydrates, particularly the rapid destruction of collector rocks during mining.

The state company Korea National Oil Corp is also engaged in the development of gas hydrate deposits; it is gaining experience by researching the process of gas production from gas hydrates in Alaska, which involves a number of American companies. The gas hydrates project is part of the state program of developing gas production in Korea, and Korean stocks of gas hydrates in the Korean sector of the Sea of Japan are estimated at \$ 1 trillion m³ of methane [9]. The process of developing these fields was scheduled to begin in 2016; and it will use the experience of extracting gas from gas hydrate deposits on land, which is likely to lead to several complications regarding the peculiarities of developing offshore fields.

The act on large-scale search and development of gas hydrates on land and at sea, passed by the US Congress in 1999, has helped investigate further extraction of gas hydrates. Inventories of gas in gas hydrate deposits in Alaska, according to preliminary estimates, amount to almost 16 trillion m³ [10]; therefore, the US primary research is carried out there. Test production of methane by the technology of replacing it with carbon dioxide was performed in 2010. In addition, since 2009, the United States Department of Energy and the private corporation Chevron have been conducting research in the Gulf of Mexico. According to the estimates by the American company Mineral Management Service, the gas hydrate reserves in the Gulf of Mexico can amount to an astronomical value of 600 trillion m³ [10].

However, so far, large oil and gas companies hesitate to develop these inexhaustible resources due to too high costs and risks. Obviously, the development of methods for extracting gas from gas hydrate deposits had paid little attention to the essential differences between onshore and offshore fields [11], although the first practical steps in this regard strongly confirm that it is impossible to transfer the experience of extracting gas from gas hydrate deposits on land to the sea as it leads to complications, mainly in the form of destroying reservoir rocks in the mining zone. Therefore, to extract gas from offshore gas hydrate deposits, it is necessary to apply certain techniques; improvement of the technological and environmental efficiency and safety requires new technological approaches.

3. Research aim and objectives

The research is aimed at identifying the peculiarities of the processes of gas extraction from marine gas hydrate deposits, namely at determining the most effective technological and ecological extraction method.

To achieve this goal, it is necessary to solve the following tasks:

 to identify the existing technological and environmental risks of the physical and chemical methods of extracting gas from marine gas hydrate deposits;

– to determine the optimal technological limits of hydrate replacement in order to optimize these processes and to prove their environmental performance.

4. Research materials and methods

4. 1. Materials for studying different ways of extracting organic gases from marine gas hydrate deposits

The study was performed through using published data [2, 5–11] on the results of various methods of extracting gas from gas hydrate deposits. The authors took into consideration the basic technological results and assessed the potential environmental risks of different methods of extracting gas from gas hydrate deposits.

4. 2. Methods of studying gas replacement modes in the gas hydrate lattice while mining

The known graphic dependencies of phase transitions of various gas hydrates were approximated by the exponential function. The integration of these functions into systems has allowed determining the limits of using various thermobaric generated gas hydrates as replacement gases.

5. The research results of technological performance and environmental efficiency of different methods of extracting gas from gas hydrate deposits

Gas hydrates as compounds include clathrates in which gas molecules are placed in a lattice consisting of water molecules held by hydrogen bonds. Gas hydrates can form and exist stably in a wide range of pressures and temperatures (for methane, from $2 \cdot 10^{-8}$ to $2 \cdot 10^{3}$ MPa at temperatures from 70 to 350 K). Some properties of hydrates are unique. For example, the total volume of water in a hydrated state integrates about 160 volumes of methane. Moreover, its specific volume increases by 26 % (in the freezing water, whereas the specific volume increases by 9 %).

Most gases, other than helium, hydrogen and n-butane, at certain pressures and temperatures in water, form solid solutions called gas hydrates or crystal hydrates. When they are formed, water molecules provide via hydrogen bonding crystal lattices [2] whose cavities contain molecules of only one specific gas, and they are held by weak van der Waals forces. Sometimes these solid solutions of gas in water are called clathrates, which means in Latin "protected by grating"; their external appearance resembles snow or neve (loose ice).

The conditions of gas hydrate formation depend of gas composition, temperature, and pressure. Usually, they are formed at temperatures below 30 °C and an increased pressure. At a temperature of 0 °C, methane hydrate is formed at a pressure of 3 MPa, ethane hydrate – at a pressure of 0.5 MPa, propane hydrate – at 0.15 MPa, carbon dioxide hydrate – at 1 MPa, and oxide hydrate – at 15 MPa. At a temperature of 25 °C, methane hydrate is formed already at a pressure of 40 MPa (Fig. 1) [2]. The density of the gas hydrates is in the range from 900 to 1,100 kg/m³.

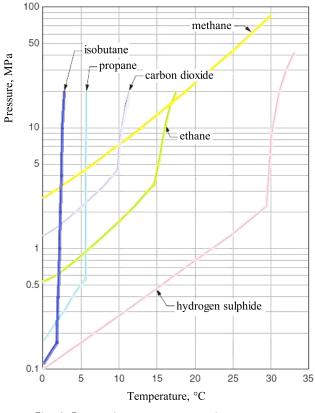


Fig. 1. Phase diagrams for some simple natural hydrate-forming gases

The conditions for their formation exist in rocks of the centuries-old permafrost zone and in the bottom layers of sea water. They correspond to 23 % of the continent, especially in Eurasia, and 90 % of the world oceans. Gas resources in these areas can be compared with reserves of free gas deposits. Hydrates can occupy about half of the permafrost that freezes to a depth of 500–1,000 m. They are found in the bottom sediments of the Baltic, Black and Caspian Seas.

In the waters of the world oceans, the hydrate formation zone begins at the bottom of the ocean and typically entails several hundred meters. Submarine deposits are confined mainly to the deep-ocean shelf and slope at depths of 200 m in the circumpolar area and from 500 m to 700 m in equatorial regions. The accumulation of natural gas hydrates on land is mainly restricted to the cooled zones of the sedimentary cover crust of the Earth. In areas of permafrost, the rock formation in which gas hydrate deposits exist can reach 400–800 m, and in some cases this value is higher than 1,000 m.

To determine the optimum process parameters in the extraction of gas from gas hydrate deposits by using the technology of replacement in the methane hydrate lattice, let us consider the schedule of phase transitions known for gas hydrates at certain temperatures and pressures (Fig. 1) [2]. For comparison, we shall consider the charts of phase transitions proposed by German experts [12] to replace methane and carbon monoxide as well as hydrogen sulphide [13].

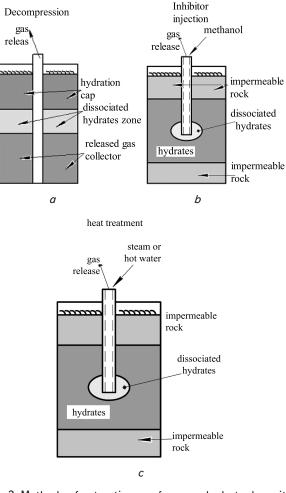
The deposits of gas hydrates, according to modern concepts, can be divided into three classes:

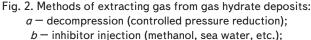
1. It consists of two layers: the actual and a lower twophase hydrate with water and free gas.

2. The hydrate layer is located above the single-phase liquid, which is water.

3. The continuous hydration layer does not have underlying water.

There are three main methods for extracting gas from gas hydrate deposits (Fig. 2).





c – heat treatment (increase in temperature)

Decompression (depression) happens due to a reduced pressure in the gas tank of a drilled well. The pressure is regulated so that hydrates decompose into components.

A thermal extraction method is based on the supply of heat to the deposit at a constant pressure.

An inhibitor input method is realized when a mineralized solution or methanol is injected into the well, which leads to a rapid release of methane due to the ratio of "pressure and temperature" being displaced from the equilibrium point.

However, the developed technologies do not exclude the occurrence of a number of problems that can lead even to an environmental disaster:

1. Difficulties of extracting methane from deposits of a crystal hydrate and the crystal hydrate cleaning of mud at big depths.

2. At a decreasing pressure and an increasing temperature during extraction, the hydrate starts to evaporate, and the methane is released in the form of uncontrolled griffins; it is dissolved in water or released to the atmosphere, which can lead to an intensified greenhouse effect [10].

3. Dissolution of the hydrate can lead to the formation of gas bubbles. When heat is supplied intensively, it can result in a so-called "gas hydrate bomb" (when pressure is reduced in the inside layer, and there happens a local explosion, with the casing destruction) or "a black hole" (if much of seam gas hydrate detaches from the bottom and emerges to the top, it quickly melts and releases a large amount of gas). It was the release of large amounts of gas that once caused the destruction of the production platforms in the Caspian Sea.

Hydrate decomposition can lead to a violation of the stability of bottom sediments on continental slopes. The sole area of gas hydrates could be a site of sharp weakening of the thickness of sedimentary rocks

Thus, any technology of mining hydrates can be successful only if it is possible to exclude additional reduction in the rock stability. Examples of complications that arise during the decomposition of hydrates can be found along the Atlantic Coast of the United States of America [10]. Here the seabed slope is 5 degrees, and in this case the bottom slope should be stable. However, there are many underwater landslide ledges. The depth of these ledges is close to the maximum depth zone of hydrates stability. This may be a sign that at present there are no hydrates here, as they have moved.

The decompression method is considered to be the most useful one because of the lowest cost of the experiments conducted in the framework of the "Research Consortium for Methane Hydrate Resources in Japan" (also known as MH21) by JOGMEC on gas production at the field Mallik (Canada) [8]; however, it can be applied only to secondary deposits, which are located on land. Moreover, in such a case, the well was drilled down to the underlying horizon of water, from which the process of reducing pressure began. After an attempt to reduce the pressure in the gas hydrate layer of the primary marine reservoir at Atsumi (JOGMEC, JAPEX, Japan Drilling) [8], the high hydrate saturation of the layer produced an entry of a large number of solid rock to the mine face, which, before the decompression, had been held down by a hydrate array. This blocked the flow of gas into the well and stopped the experiment.

In 2002, the method of heat treatment was also tested in the Mallik gas hydrate field [14]. Water heated up to 80 °C was pumped into the hole that was 1,100 m deep. The yield was only 470 m^3 of gas, which clearly indicated a low technological efficiency of the method. Besides, this method can not be used at big depths, as the depth rapidly decreases the coolant temperature.

The method of injecting inhibitors – such as methanol, ethanol, glycol, and salt solutions, including seawater – currently is not used in practice in view of a known high ecological risk of most of these substances and the slow progress of such chemical reactions.

Moreover, mining of secondary marine deposits by all methods can be dangerously destructive for the seabed. The only option of the chemical method of gas extraction from gas hydrate deposits is a method of replacing methane in the hydrate with another hydrate-forming gas, which can ensure protection of the general structure of the deposit from destruction and can help dispose of hazardous gases such as carbon dioxide and hydrogen sulphide.

To implement this method of extracting methane from gas hydrate deposits, it is necessary to create imbalanced thermobaric conditions in the current range of the mining pressure. The reduction of pressure and the input of heat are restricted to the lower limit of gas content in water and the coolant's temperature. The temperature of the coolant is regulated with regard to the estimated value at the exit point of the coolant in the open borehole. Then seawater is periodically pumped inside along with the dissolved natural hydrogen sulphide.

In the Black Sea, there is an abnormal gas mode in which the concentration of hydrogen sulphide in the water rises to 14 ml/l. The only currently conducted experimenting with gas extraction from marine gas hydrate deposits around Atsumi Peninsula (Japan) [8] has showed the presence of hydrate content of about 70 % in the rock, which can result in a possible drawdown of the bottom soil as methane hydrates are also contained in the skeleton of the underlying bottom soil. Besides, the decomposition of gas hydrates will reduce the reservoir properties of the mine face zone due to particulate contamination. Therefore, reservoir rocks of the marine deposits should be consolidated. The easiest way to do this is to combine the processes of gas extraction and replacement of methane with another hydrate-forming gas.

According to the patented method [13] (Fig. 3), from the maritime platform (2), a hole (1) in drilled into the well (1). The well is isolated from the surrounding seawater by a sealing (waterproof) column (3), which contains a launched production string (4). It has perforated holes (5) and includes a horizontal portion of the gas hydrate layer (6). The tubing (11) holds a mounted ejector pump (9) with a packer (10) to be lowered into the well (1) at the estimated depth. The well (1) from the face (7) to the mouth (8) on the platform (2) is filled with sea water. The intercolumn (12) between the production string (4) and the tubing (11) is pressurized with the packer (10).

Down to the estimated depth of the cavity of the tubing (11), a flexible coil pipe (13) is drained, with a cavitation chamber (14) connected to the lower end thereof. It is placed in the area of the gas hydrate occurrence.

The forcing of the working fluid in the form of sea water under the estimated pressure into an annular space (15) starts the workflow of extracting methane. Hereby, the hydrate starts transforming from a solid to a liquid state, which is an aqueous solution due to the changing temperature and pressure conditions. For the extraction pressure in the gas hydrate layer (6) to be equal to or above the pressure of the water saturated with gas, the working pressure in the ejector pump (9) is maintained so that the gas does not get separated from the water. Water with dissolved gas begins to penetrate into the annular space (16) and moves towards the ejector pump (9).

The destruction of the gas hydrate combines with an endothermic reaction, i.e. absorption of the energy. The temperature in the reservoir of the gas hydrate (6) begins to decrease, which in turn can lead to the formation of gas hydrates from the liquid phase. To avoid this in the flexible coil tubing (13), seawater is injected as a coolant. The coolant injection is performed under the estimated pressure. After passing through the cavitation chamber (14) under the influence of the cavitation process, the coolant is heated to the calculated value. Moreover, the extent of the heat in the coolant is regulated by the pressure of the coolant injection into the flexible coil tube (13). This regulates the compensation of the heat that is absorbed in the endothermic reaction of the decomposition of gas hydrates. The coolant, having performed its function, gets mixed with the liquid phase of the gas hydrate and enters the annular space (16), moving towards the ejector pump (9). In the ejector pump (9), the well output, together with the coolant, mixes with the working fluid of the ejector pump (9) and then enters the annular space (12) by which the whole mixture rises to the surface of the platform (2).

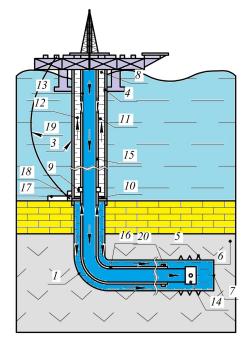


Fig. 3. Extraction of gas from gas hydrate deposits by replacing the hydrate-forming gas in the reservoir:
1 - the well; 2 - the platform; 3 - a waterproof column;
4 - the production string; 5 - perforated holes;
6 - the gas hydrate layer; 7 - the face; 8 - the mouth of the well; 9 - an ejector pump; 10 - a packer;
11 - a pump tubing; 12 - an intercolumn space between the production string and the pump tubing; 13 - a coil tubing pipe; 14 - a cavitation chamber; 15 - an intercolumn space between the coil tubing pipe and the pump tubing;
16 - a reverse flow at the bottom of the intercolumn space 15; 17 - a bottom pump; 18 - the bottom blowout prevention equipment; 19 - a hosecable

After rising to the surface, the mixture of water and gas is split. Excess of water is discharged into the sea, and the gas goes into further processing for transporting to the shore. The operation dissolves a significant amount of hydrates, which also hold the overall structure of the collector. To ensure the stability of the latter, the dissolved hydrates should be partially replaced. Hydrogen sulphide hydrates exist at lower pressures, which allow further development of the deposit beyond the thermodynamic equilibrium of hydrate hydrogen sulphide existence. To this end, after the termination of the periodic removal of methane, the bottom sea water with a high content of hydrogen sulphide is supplied through the underwater blowout preventer equipment (18) that is connected via a bottom pump (17) which is controlled from the surface by an underwater hose-cable (19). To prevent early hydrate formation in the pre-calculated sections of the pump tubing column, ultrasonic dispersers are installed. To reduce corrosion of hydrogen sulphide, fiberglass pump tubing is used.

A similar technology can be applied in the case of using carbon dioxide as a hydrate-replacing gas. However, it is necessary to note that its supply from the surface requires additional equipment in the form of storage tanks and gas reducers. This helps remove the bottom pump from the circuit but requires an additional column for supplying the hydrate-replacing gas from the surface.

Effective and safe gas extraction can be ensured by controlling the formation of a new replacing gas hydrate and the destruction of methane hydrate. This problem is solved by using phase transition charts (Fig. 1) that contain technological criteria planes in which, with a decrease in pressure and an increase in temperature, methane hydrates do not exist any more, and hydrates of hydrogen sulphide and carbon dioxide are formed. Let us determine the effectiveness of various hydrate-replacing gases.

When transferring the data of the graphs from the exponential scale into a natural one, we get the curves of gas hydrate phase transitions dependence on pressure and temperature (Fig. 4).

Since in the exponential scale the data curves were straight lines, they can be approximated by exponential functions. The method of least squares can help obtain the exponential functions of hydrate phase transitions for various hydrate-forming gases. The standard deviation for each function is less than 3 %, indicating an adequacy of correlation between the derived functions and real processes. Thus, we have obtained the descriptions of the hydrate phase transitions:

(1) methane:

$$P_{\rm CH_{c}} = 1.2193 \cdot e^{0.4981 \cdot t}; \tag{1}$$

(2) hydrogen sulphide:

$$P_{H_{LS}} = 0.037 \cdot e^{0.5356t};$$
(2)

(3) carbon dioxide:

$$P_{CO_{a}} = 0.4086 \cdot e^{0.5854t}, \tag{3}$$

where P is the pressure of the phase transition, MPa; t is the temperature, $^\circ C.$

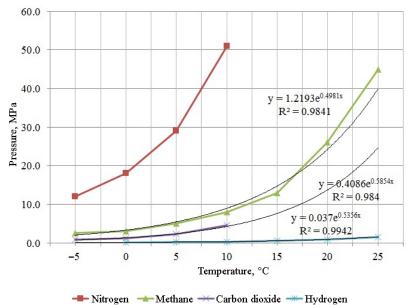


Fig. 4. The curves of hydrate transformations in the natural scale

The plane between the curves of phase transitions in Fig. 4 is an area where methane hydrate can not exist, but hydrates of other gases do exist. Thus, the data of the plane for the combinations of methane-replacing gases are the technological scope of using these gases.

The technological plane for replacing methane with hydrogen sulphide $D_{(H_2S-CH_4)}$ can be represented by respective borders, using the equations (1)–(3) and temperature limits on the existence of these hydrates (Fig. 1, 4):

$$P \leq 1.2193 \cdot e^{0.4981t}$$

$$P \geq 0.037 \cdot e^{0.5356t}$$

$$t \geq -5$$

$$t \leq 25$$

$$P \leq 0.037 \cdot e^{0.5356t}$$

$$P \leq 0.037 \cdot e^{0.5356t}$$

$$P \geq 0.037 \cdot e^{0.5356t}$$

The technological plane for replacing methane with carbon dioxide $D_{(CO_2-CH_4)}$ has other temperature limits on existence of such hydrates (Fig. 1, 4):

$$\begin{array}{c} P \leq 1.2193 \cdot e^{0.4981 t} \\ P \geq 0.4086 \cdot e^{0.5854 t} \\ t \geq -5 \\ t \leq 10 \end{array} \right\} D_{(CO_2 - CH_4)}.$$
(5)

For comparing the technological and environmental safety of various methane-replacing gases, it is necessary to determine the areas of these technological planes (4) and (5) by integrating them within the relevant temperatures in which such hydrates exist:

- for the technological plane $D_{(H_2S-CH_4)}$

$$S_{D(H_2S-CH_4)} = \int_{-5}^{25} (1.2193 \cdot e^{0.4981t} - 0.037 \cdot e^{0.5356t}) dt =$$

= 581251.33, (6)

- for the technological plane $D_{(CO_2-CH_4)}$

$$S_{D(CO_2-CH_4)} = \int_{-5}^{10} \left(1.2193 \cdot e^{0.4981t} - - - 0.4086 \cdot e^{0.5854t} \right) dt = 112.96.$$
(7)

The obtained values of the conventional parametric spaces of the technological planes show that the use of hydrogen sulphide as a hydrate-replacing gas during the extraction of gas from hydrate gas deposits are by several orders technologically and environmentally safer compared to carbon dioxide. However, in the waters of a normal gas regime it is necessary to take into account the absence of natural hydrogen sulphide. Thus, the transportation and use of hydrogen sulphide in vessels at high pressure can complicate labour protection measures. Therefore, in this case, it is possible to use carbon dioxide as a hydrate-replacing gas.

6. Discussion of the research results on the technological performance and environmental efficiency of various methods of extracting gas from gas hydrate deposits

An especially important result of the study is that by analysing different methods of extracting gas from gas hydrate deposits there appears an opportunity to determine the best method for different fields:

– for primary marine gas hydrate deposits, one of the most technologically and ecologically expedient methods is the replacement of hydrate-forming gases [11], which allows retaining the overall skeleton of the rocks without destroying it;

– for secondary terrestrial deposits, a more optimal solution is a method of controlled decompression [15], since with the overall maintaining of the solid rock structure in which the pores release the hydrate this method does not require large expenditures on materials (often harmful to the environment) and equipment.

The advantage of this study is the fact that after comparing the estimates for the conventional areas of the technological planes of hydrate-forming gases (6) and (7) it can be argued that the replacement of methane with hydrogen sulphide in hydrate deposits is by several orders technologically and environmentally safer than using carbon dioxide. This is especially important in the practice of extracting gas while controlling the process of the replacement in terms of the layer when the process parameters are usually impossible to adjust accurately through its various individual properties. However, the findings do not deny the possibility of using carbon dioxide as a hydrate-replacing gas.

When using the obtained results in practice, it is also necessary to take into account the effect of self-conservation [16] and heat loss during the movement of gases and solutions in the columns of the well.

The drawback of the study is that the possibility to adjust the porosity and permeability of the obtained hydrates replacement remains unproven, although it would determine the intensity of the subsequent replacement of hydrate-forming gases at a greater distance from the bottom of the well and its flow rate. With some probability, it can be argued that maintaining the required properties of hydrates substitution can be achieved by compliance with certain ratios of the volumes of the substitute hydrate-forming gases and the existing water. Further studies should also take into account the solids content in such gas hydrate deposits.

An additional effect of the use of the replacement technology at extracting gas from gas hydrate deposits might be the utilization of the dangerous greenhouse gas, which is carbon dioxide. This additional effect can be assessed only after determining the dependencies in streamlining the process of substitution. It is necessary to determine the correlation between the hydrate-forming gas and the available water in which the rock strength allows withstanding the existing pressure in the reservoir and the resulting porosity and permeability, which correspond to the maximum flow rate of methane.

7. Conclusion

1. The analysis of the existing practical results to determine a technologically and environmentally effective method of extracting gas from gas hydrate deposits has revealed that a distinction must be made between primary (marine) and secondary (land) deposits. It has been determined that in developing primary resources the optimum method is to replace hydrate-forming gases, and in developing secondary resources it is expedient to use the controlled decompression method. Whereas the first method allows maintaining the overall structure of the rocks by creating a hydrate on the basis of another hydrate-forming gas (hydrogen sulphide or carbon dioxide) instead of methane, the second is economically and technologically more reasonable but applicable only to terrestrial deposits. When extracting methane from gas hydrate deposits of the first type, environmental risks of landslides (of the bottom soil and the underlying rocks) and fugitive methane emissions can be prevented only through the formation of another hydrate with the required properties. The second method requires no additional costs for the injection of various substances in the deposit layer.

2. The method of technological planes was used for a complete technical and environmental effect of the replacement method. The study has proved effectiveness of two different gas hydrate substitutions – hydrogen sulphide and carbon dioxide. Adjustment of the technological parameters of the substitution process in the gas hydrate reservoir under imperfect geological information requires quite a wide range of possible values of these parameters. The undertaken research has revealed a greater adaptability and, therefore, environmental efficiency of hydrogen sulphide as a hydrate-replacing gas at extracting methane from marine deposits of gas hydrates.

References

- Makogon, Y. Natural gas-hydrates A potential energy source for the 21st Century [Text] / Y. Makogon, S. Holditch, T. Makogon // Journal of Petroleum Science and Engineering. – 2007. – Vol. 56, Issue 1-3. – P. 14–31. doi: 10.1016/j.petrol.2005.10.009
- Kvamme, B. Thermodynamic implications of adding N₂ to CO₂ for production of CH₄ from hydrates [Text] / B. Kvamme, T. Kuznetsova, A. Sapate, K. Qorbani // Journal of Natural Gas Science and Engineering. – 2016. doi: 10.1016/j.jngse.2016.03.095
- Archer, D. Ocean methane hydrates as a slow tipping point in the global carbon cycle [Text] / D. Archer, B. Buffett, V. Brovkin // Proceedings of the National Academy of Sciences. – 2009. – Vol. 106, Issue 49. – P. 20596–20601. doi: 10.1073/pnas.0800885105
- Femyak, Y. M. Gazogidraty Cheornogo morya [Text] / Y. M. Femyak, O. Yu. Vytyaz, Y. Y. Yakimechko, S. O. Oveckii // Offshore. 2014. – Vol. 3. – P. 16–20.
- Zhang, H.-t. Survey and research on gas hydrate inpermafrost region of China [Text] / H.-t. Zhang, Y.-h. Zhu // Regional Geology of China. – 2011. – Vol. 12. – P. 1809–1815.
- Bi, Y. Thermodynamic optimization for dissociation process of gas hydrates [Text] / Y. Bi, J. Chen, Z. Miao // Energy. 2016. Vol. 106. – P. 270–276. doi: 10.1016/j.energy.2016.03.029
- Chong, Z. R. Review of natural gas hydrates as an energy resource: Prospects and challenges [Text] / Z. R. Chong, S. H. B. Yang, P. Babu, P. Linga, X.-S. Li // Applied Energy. – 2016. – Vol. 162. – P. 1633–1652. doi: 10.1016/j.apenergy.2014.12.061
- Yamamoto, K. Overview and introduction: Pressure core-sampling and analyses in the 2012–2013 MH21 offshore test of gas production from methane hydrates in the eastern Nankai Troug [Text] / K. Yamamoto // Marine and Petroleum Geology. – 2015. – Vol. 66. – P. 296–309. doi: 10.1016/j.marpetgeo.2015.02.024
- Scientific Results of the Second Gas Hydrate Drilling Expedition in the Ulleung Basin (UBGH2), East Sea of Korea [Text] / B.-J. Ryu, M. Riedeland, T. S. Collett (Eds.) // Marine and Petroleum Geology. – 2013. – Vol. 47. – P. 1–302.
- Vedachalam, N. Review of unconventional hydrocarbon resources in major energy consuming countries and efforts in realizing natural gas hydrates as a future source of energy [Text] / N. Vedachalam, S. Srinivasalu, G. Rajendran, G. A. Ramadass, M. A. Atmanand // Journal of Natural Gas Science and Engineering. – 2015. – Vol. 26. – P. 163–175. doi: 10.1016/j.jngse.2015.06.008
- Chen, J. Energy-efficient methods for production methane from natural gas hydrates [Text] / J. Chen, Y.-H. Wang, X.-M. Lang, S.-S. Fan // Journal of Energy Chemistry. – 2015. – Vol. 24, Issue 5. – P. 552–558. doi: 10.1016/j.jechem.2015.08.014
- Deusner, C. Methane Production from Gas Hydrate Deposits through Injection of Supercritical CO₂ [Text] / C. Deusner, N. Bigalke, E. Kossel, M. Haeckel // Energies. – 2012. – Vol. 5, Issue 12. – P. 2112–2140. doi: 10.3390/en5072112
- Patent № u 201405395 na korysnu model'. Sposib intensyfikacii vydobuvannia metanu z tverdykh gazovykh gidrativ piddonogo zalyagannia z zakriplenniam [Text] / Vytyaz O. Yu., Oveckii S. O., Femyak Y. M., Todorchuk A. F., Say K. S. – Ukraine, MPK E21B43/00, 2014. – 5 p.
- Dallimore, S. R. Four decades of gas hydrate research and development at Mallik site, Mackenzie Delta, Northwestern Territories, Canada [Text] / S. R. Dallimore, K. Yamamoto, F. Wright // Presentation held at the 'International Symposium on Methane Hydrate Resources – from Mallik to Nankai Trough' in Tokyo, 2010.
- Patent № u 201405379 na korysnu model'. Sposib vydobuvannia metanu z tverdykh gazovykh gidrativ [Text] / Vytyaz O. Yu., Oveckii S. O., Femyak, Y. M., Todorchuk A. F., Levchenko V. S. – Ukraine, MPK E21B43/00, 2014. – 5 p.
- Pavlenko, A. Study of the stability of methane hydrates in normal conditions [Text] / A. Pavlenko, O. Vytyaz, H. Koshlak // AGH Drilling, Oil, Gas. – 2014. – Vol. 31, Issue 4. – P. 495–507. doi: 10.7494/drill.2014.31.4.495