






# An alternative method of methane production from deposits of subaquatic gas hydrates

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## Abstract

**Purpose.** Determination of the potential efficiency of the alternative method of methane production from subaquatic gas hydrate deposits using the emissions of underwater mud volcanoes considering geological and thermodynamic conditions typical for the Black Sea.

**Methods.** Computer modeling of the processes considering changing of the thermodynamic parameters of the supplying fluid within the pipeline and hydrate deposits was carried out on the basis of the Aspen Hysys program, using the Ng and Robinson model to calculate the energy potential of the fluid.

**Findings.** An algorithm for calculating the distance to which a flow of the emissions mud volcano can be delivered with a temperature sufficient to remove sea bed hydrates from thermodynamic equilibrium and release methane has been developed. The schematic technological solution of an alternative method of methane production from gas hydrate deposits were presented by using the energy of emissions of mud volcano (fluid). The collection device for emissions of mud volcano and gas hydrate sea bed deposits were also been used within the model. The calculations have been done using Aspen Hysys computer program.

**Originality.** The potential efficiency of the alternative method of methane production from gas hydrated sea bed deposits using thermal energy from emissions of underwater volcanoes is substantiated. It is also shown that in the case when the hydrate deposits cover the sea bed natural gas deposits as an impermeable layer, the thermal energy of the gas flow extracted from the sea bed natural gas deposits can be used for the decomposition of the hydrates This case is similar to the considered alternative method of using thermal energy of the emissions of mud volcanoes.

**Practical implications.** The use of an alternative method of methane production from gas hydrate sea bed deposits by using emissions of mud volcano make it possible to increase the amount of gas obtained from subaquatic sources ~ by 7-10% without using additional sources of thermal energy. The practical application of this method will also prevent methane emissions from mud volcanoes into the atmosphere, which reduces pollution of seas and oceans with dissolved gases.

**Keywords:** methane, deposits of subaqueous gas hydrates, underwater mud volcanoes, fluids, underwater pipelines, fluid thermodynamic parameters

## 1. Introduction

Modern studies testify to the great potential of methane hydrate deposits to provide energy to humanity in the near future [1], [2]. At the same time, it should be considered a proven fact of reducing the environmental impact of the energy industry due to the use of methane, instead of coal and oil refining products, and also the possibility of utilizing carbon dioxide by burying it in the form of hydrates when replacing methane in the process of extracting hydrate deposits [3]. The significance of hydrate technology for CH<sub>4</sub> production and CO<sub>2</sub> utilization is also that widely used such technology can even change the nature of the planetary carbon cycle and reduce the likelihood of a catastrophic global warming scenario [4]. However, the currently available modern technologies for extracting methane from hydrate de-

posits are characterized by a number of possible environmental and economic problems [5]-[7]:

1. As a result of the dissociation of methane deposits, a mixture of a high content of mechanical and chemical impurities rises to the surface, which makes its mandatory to use complex and expensive methods for cleaning well products.

2. The formation of gryphons of artificial origin due to the passage of dissociated methane outside the casing, the cause of which is the loss of control of mining operators over the propagation of the front of destruction of hydrate inclusions. This can lead to continuous leakage of the greenhouse gas methane into water and the atmosphere.

3. The formation of uncontrolled gas bubbles at the sea bed or near-well area is possible. This can lead to an explosion with catastrophic consequences.

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4. Sea bed sediments are usually unstable even to small displacements. When the skeleton of the rock is lost due to the decomposition of marine massive gas hydrates, displacement and subsidence of the sea bed soil are possible. This can lead to a possibility of earthquakes, which in their consequence can format and propagation of non-periodic high and powerful waves.

Therefore, as noted, one of the safe technologies for extracting methane from gas hydrate deposits includes substitution methane with carbon dioxide or other hydrate-forming gases [5]. The main technological problem in the implementation of this extraction method [6] is the need to maintain thermodynamic conditions within the near-well zone in the range of characteristics, which allow replacement methane (with carbon dioxide, hydrogen sulfide etc.), while methane-hydrates are destroyed and cannot keep methane within its structure. The future fate of this method depends on the possibility of forming a sufficient level of permeability for methane replacement. That will allow methane to be extracted considering the increase of the radius of the supply circuit. Such technology can be classified as a variant of a physical-chemical method of methane production from hydrate deposits.

Other methods are combined according to general classification features of impact on the formation into physical and mechanical. The latter are considered not very promising, as they require underwater pit works, which makes them unprofitable.

Among the physical methods, we can identify the method of pressure reduction, which showed its effectiveness at development of the Messoyakh field. Although, this method, did not live up to expectations at development of the Nankai marine hydrate field. We think this is related to the main features of marine (primary [1]) and upland (secondary) hydrate deposits. Those features are different due to different structure and the presence of various structure-forming elements (structure-forming elements are hydrates itself for primary hydrate deposits and different sedimentary rocks – for secondary). Thus, when the pressure within marine hydrates decreases, small inclusions of sedimentary rocks, as well as large volumes of impurities of solid rock particles placed around the hydrate crystals, during its destruction and intensively accumulated at the sea bed of the well and in the near-well zone and reduce gas flow to zero.

Numerous thermal methods of gas production from gas hydrate deposits have shown their economic cost-effectiveness during experimental tests in the area of the upland Mallik deposit [8]. However, in our opinion, their application for marine hydrate deposits can be improved.

Known factors [1]-[4], [9] that determine the formation mechanism of gas hydrate deposits are:

- a) the thermodynamic regime of rocks at the sea bed and below the sea bed of this water area;
- b) the intensity of generation and migration of hydrocarbons;
- c) the composition of gas;
- d) the degree of gas saturation and mineralization of reservoir waters;
- e) the structure of porous environment;
- f) lithological characteristics of the section;
- g) geothermal gradient in the zone of hydrate formation;
- h) in the underlying rocks, phase state of hydrate formation, etc.

A significant quantity of hydrocarbons generated at sea bed sedimentary rocks are not dispersed, but accumulated in the form of hydrates, even in the absence of lithological

seals. This fact indicates the inseparability of the process of hydrocarbon genesis and the formation of gas hydrate deposits in the waters of the World Ocean.

The upper limit of the zone of hydrate formation in water areas is mainly located in the water column, the lower – in rocks [1]. Based on the thermal characteristics of the deep-sea area of the ocean, as well as the facts of the accumulation of most of the sedimentary rocks and organic matter in the peripheral area of the ocean, deep-sea shelf sediments and sediments of the continental slope should be considered the most promising zones of hydrate distribution. As for the abyssal zones of the huge ocean plain, the sediments here are poor in organic matter, the geothermal gradients are high, so there is no reason to associate with them serious prospects for the accumulation of hydrates (if we do not consider the possibility of the inorganic origin of hydrocarbons) [5].

Gas hydrate deposits are formed in the zone of hydrate formation during the period of sedimentation from the upper boundary of the zone, as a result of the arrival of new portions of organic matter in the initial period of its transformation. They are form the lower boundary with help of gases, which are formed in subsequent periods of deepening and further transformation of organic matter, as well as gases coming from the deep bowels of the Earth. The vertical migration of gas from the primary zones of gas formation (high temperature) to the zone of hydrate formation increases the thickness of deposits from below. Also, free gas can be accumulated beneath formations that contain hydrates. These gas deposits can be developed by conventional methods, given the presence of a gas hydrate seal. There are also known cases when oil deposits are formed under hydro-saturated layers [10].

The stable existence of gas hydrate deposits within continents and water areas are ensured by fundamentally different conditions. Since the temperature of sea water areas changes only within a relatively small layer of surface water, gas hydrate deposits formed in a deep-water area are almost not affected by temperature changes of the water surface. Even with a significant increase in near-surface temperatures, the temperature in a deep water (where gas hydrate may be created) remains practically unchanged [11].

Gas hydrate deposits in water area are obviously subject to the influence of changes of level of the World Ocean, caused by alternating processes of global warming and glacial periods over a long geological time. Gas hydrate deposits are found at different depths: from several hundreds or even tens of meters from the water surface [12], due to a decrease in pressure at the depth of the water area as a consequence due to glaciation (possible additional factor can be tectonic and stratigraphic movements). During the ice Age, the level of the World Ocean substantially decreased with practically unchanged deep-water temperatures. As a result of such changes, hydrate decomposition occurred within sea bed sediments. When the hydrate decomposes, the gas partially migrates into the atmosphere, contributing to the greenhouse gas effect. Also, gas, which is coming from under sea bed and accompanied by rock particles, forms, so-called, underwater volcano's mud. Such event can happen constantly or periodically [13]. Natural gas from underwater mud volcanoes does not form hydrates due to the lack of necessary conditions. However, hydrates are often present at a short distance from underwater mud volcanoes, as the presence of the former is very often a sign of sea bed and sub-sea bed gas hydrate deposits.

Considering above mentioned properties of gas hydrate deposits three main methods for methane production can be practically implemented:

- 1) injection of under pressure warm water into the well (thermal method);
- 2) lowering pressure within gas hydrate layer;
- 3) introduction of CO<sub>2</sub> (or a mixture of CO<sub>2</sub> and N<sub>2</sub>) into the gas hydrate layer to replace methane gas [8].

Technologies that use these methods are based on a general principle: disturbance of the equilibrium state of gas hydrates in the layer, as a result of which the thermodynamic stability of the gas hydrate is lost and it decomposes into methane and fresh water. Each of the above methods has its own advantages and disadvantages. However, but the main disadvantage of all of them is the high consumption of energy. The required amount of energy may be comparable to the energy that can be obtained from the use using extracted gas as a source of energy [14]. First of all, it is related to the thermal method.

As known, part of the deposits of subaqueous gas hydrates are located in the water area of oceans and seas, where the surface water has a temperature of 20-28°C, and the main mass of water at depth has a temperature of 4-10°C [15]-[17]. In such cases, it is possible to increase the energy efficiency of methane extraction by using Ocean Thermal Energy Conversion (OTEC) technology [18]. If sea bed deposit of methane-hydrates is located at the edge of mud volcanoes (for example such conditions exists at Black Sea [13], [19], the efficiency of thermal method of methane extraction can be improved by using the energy of underwater mud volcanoes. Such improvement was proposed by authors of [20]. Implementation of this method, in contrast with previously proposed method [6], allow also solve the issue of effective use of mud volcanoes gas to reduce environmentally harmful emissions of methane to the atmosphere. Although, the economic expediency of using gases from mud volcanoes may be questionable due to the fact that the gas productivity of mud volcanoes has not been studied. Some authors [21] claim that the volume of such emissions is small and corresponds to the characteristics of methane seeps, namely 0.01 l/min. However, others authors [22] estimate such emissions within the range of: 509.8-550.0 l/min for areas of Sorokin's deflection. Wherein at the initial depths, which correspond to the minimum thermodynamic conditions of the sea bed occurrence of hydrates, productivity is higher to the order of magnitude. So, the purpose of this study is to prove the effectiveness of using the energy from underwater mud volcano to extract methane from subaqueous hydrate deposits.

The task of this study is to develop a methodology for calculating the potential of an underwater mud volcano as an energy source for removing sea bed hydrates from thermodynamic equilibrium. The author's task is also to determine by use of computer modeling the potential for implementing an alternative method of methane extraction from underwater gas hydrate deposits. The geological and thermodynamic conditions of this work correspond to Black Sea deposits.

According studies [13], the distance between the sea bed of hydrate deposits and mud volcanoes does not exceed 1.5 km due to a certain structure of mud volcano and neighbouring natural gas outlets where formation of gas hydrate deposits are very likely (Fig. 1) [23].

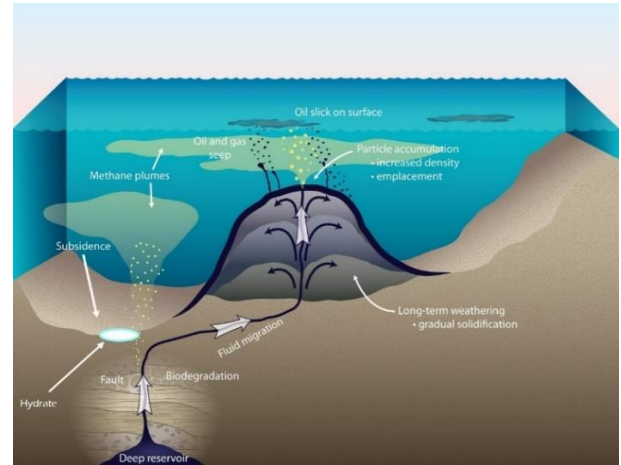


Figure 1. Diagram of an underwater mud volcano (the authors also show the location of sea bed hydrates)

The amount of gas hydrate deposits around a mud volcano primarily depends on the geological conditions of its location and the temperature and pressure of water at the level of the hydrate deposits. For example, according to the authors [24], the volume of sea bed hydrate deposits around the Odesa mud volcano in the Black Sea can be estimated at  $1 \cdot 10^6$  m<sup>3</sup>, and the amount of methane within it is around  $\sim 1.8 \cdot 10^8$  m<sup>3</sup>.

An alternative method of gas production from gas hydrate deposits is proposed by [20], using the energy of mud volcano emissions (fluids) to remove gas hydrates from thermodynamic equilibrium and release methane. A schematic technological solution for the implementation of this method, is shown in Figure 2. According this picture the products of mud volcano emissions are collected with the help of gas collection devices 3 and directed to gas hydrate deposits through an underwater pipeline 6. For example, devices 3 can be made in the form of the structure given in [25].

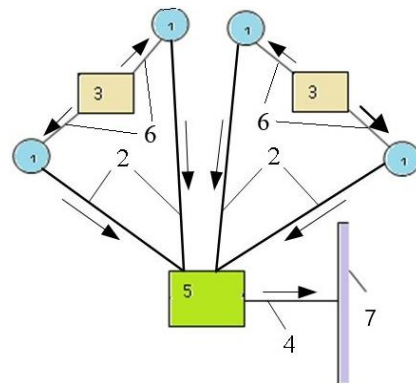


Figure 2. Schematic technological solution of an alternative method of methane production from gas hydrate deposits by using the energy of mud volcano emissions (fluids): 1 – sea bed gas hydrate deposits; 2 - pipelines for supplying gas extracted from gas hydrate deposits; 3 – collection device for fluid emissions on a mud volcano; 4 – gas supply loop to the main pipeline; 5 – floating vessel for gas production, storage and offloading (FPSO); 6 – fluid supply pipeline to hydrate deposits 7 – underwater main gas pipeline

## 2. Methods

To calculate the energy of the potential fluid it is appropriate to use the Ng and Robinson model [26]. This model allows consider the multicomponent composition of mud

volcano emissions. The model calculates thermodynamic parameters and flow characteristics during the movement of multiphase fluids in pipelines considering possible hydrate formation [27]-[29]. The HYSYS package was used for computer simulation. This package is a contemporary software information system for the processes of chemical technologies and includes:

- ways of description and editing of technological diagrams;
- a database for calculating the properties of individual components and their mixtures;
- methods for calculating the physical characteristics of hydrocarbon fractions;
- a library of typical models of apparatuses for chemical technologies;
- a set of mathematical methods for calculation and optimization of technological systems;
- tools for viewing reference information and tools for processing results.

The system allows data editing operations by several alternative ways (using tabular or graphic form from the menu or selected keys, etc.). Such flexibility lets each user to choose the most convenient working method. In addition, the package presents the open system and let the user a possibility to connect to the system new software modules.

To model the technological process the system requires:

- a) to describe the set of devices used within the process and their connection (switching) scheme;
- b) to specify the characteristics of raw material flows and product quality requirements;
- c) to specify the range of permissible control influences, etc.

Input above mentioned information to the model has two aims. The first aim is connected to meaningful essence of conducted research. The second aim is connected to the formal rules of coding and editing of output information, namely: consequence of output information, to which tables or which forms the will be output, dimensions of the output results, how diagnostics messages will be issued, etc.

Considering the above mentioned the following technique is used to determine the working efficiency of the alternate method of methane production from subaqueous of gas hydrates from subaqueous deposits of gas hydrates deposits (the calculations are made for the gas component):

1. The Reynolds number, showing the thermodynamic of flow's regime from the mud volcano, is determined. The fluid is directed from collection device 3 to gas hydrate deposit 1 through pipeline 6 (Fig. 2).

2. Determine Froude's and Euler's numbers.

3. Calculate the internal diameter of the pipeline at the specified speed of the volcanic fluid according to its flow at the operating pressure and temperature. After that determine the actual value of the internal diameter of the gas pipeline according to the tabular data. Considering the maximum value of the working pressure inside gas pipeline and its thickness the actual speed of the volcanic fluid in the pipeline is calculated.

4. The pressure at the end of the pipeline can be determined by the formula:

$$p_f = \sqrt{p_s^2 - \frac{Q^2 \cdot \lambda \cdot \Delta\rho \cdot T_{av} \cdot z_w \cdot l}{10,23 \cdot 10^{-12} \cdot d_{in}^5}}, \quad (1)$$

where:

- $p_s$  – volcanic fluid pressure at the beginning of the pipeline, MPa;
- $\lambda$  – coefficient of hydraulic resistance of the gas pipeline;
- $T_{av}$  – average temperature in the pipeline, K;
- $z_w$  – the coefficient of super compressibility of the fluid in working conditions;
- $l$  – length of the gas pipeline, km;
- $\Delta\rho$  – the relative density of the fluid at normal conditions.

5. With known value of  $p_f$  the pressure at a given section of the flow line is determined by the Formula:

$$p_x = \sqrt{p_s^2 - \left(p_s^2 - p_f^2\right) \cdot \frac{x}{l}}, \quad (2)$$

where:

$x$  – distance from the beginning to the settlement point of the gas pipeline, km.

It should be noted that the value  $T_{av}$  within the temperature range at which the fluid is transported from the mud volcano to the gas hydrate deposit, practically does not affect the value  $p_f$ , which is determined by Equation 2. The value  $T_{av}$  can be found as the arithmetic mean between the temperature of the fluid at the beginning of the flowline and the soil temperature at the depth of the pipeline when calculating  $p_f$ .

6. During transportation, the temperature of the volcanic fluid changes due to the reduction of pressure and heat exchange with the environment. The temperature of the fluid is calculated by the Equation:

$$T = T_g + (T_s - T_g) \cdot e^{-al}, \quad (3)$$

where:

- $T$  – is the fluid temperature at the calculated section  $l$ , K;
- $T_s$  – is fluid temperature at the initial section of the pipeline, K;
- $T_g$  – is environment temperature at the depth of the pipeline, K;
- $a$  – is Shukhov's parameter, which is calculated by the formula [28], [29].

7. The amount of heat  $Q_{fl}$ , that obtained from volcanic fluid when reached deposit to melt subaqueous gas hydrates is determined by the Expression:

$$Q_{fl} = G_{fl} \cdot c_{fl} \cdot (T_s - T_{fl}), \quad (3)$$

where:

- $G_{fl}$  – is mass flow rate of fluid, kg/h;
- $c_{fl}$  – is heat capacity of the fluid, kJ/kg·K;
- $T_s, T_{fl}$  – are temperature at the beginning and end of the fluid pipeline, K.

8. The amount of gas  $G_{h,m}$ , obtained from melted gas hydrates is calculated by the Expression:

$$G_{h,m} = \frac{Q_{fl} \cdot S_h}{\Delta H_h}, \quad (3)$$

where:

- $S_h$  – is the mass concentration of gas hydrates in the deposit, kg/kg;
- $\Delta H_h$  – is specific heat of fusion of gas hydrates, referred to 1 kg of emitted gas, kJ/kg of gas.

To simplify the calculations, we take the value of  $\Delta H_h$ , equal to corresponding value for methane.

The initial data for the simulation are taken from Tables 1 and 2.

**Table 1. Component composition of gas for mud volcano “Odesa”**

Component composition of gas, volume percentages (%)								
gas	CH <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	CO <sub>2</sub>	He	N <sub>2</sub>	H <sub>2</sub> S
%	94.5	1.15	1.4	0.6	0.85	0	1.25	0.25

**Table 2. Initial data for the modeling of operation of the underwater fluid pipeline**

Underwater volcano	Odesa
Temperature at the beginning of the fluid pipeline, °C	57
Pressure at the beginning of the pipeline, MPa	25
Length of the pipeline, m	2000
Diameter of the pipeline, mm	114
Geodetic difference marks, m	-100
Fluid flow rate, thousand m <sup>3</sup> /d	29.17
Water temperature, °C	+9
Absolute roughness of pipes, mm	4.572·10 <sup>-5</sup>
	Polyurethane (in water)
	Bitumen (in water)
Type of insulation and type of environment of the pipeline	Polystyrene (in water)
	Polystyrene (in sea bed clay)
Insulation thickness, mm	10
Melting point of the hydrate at geodetic difference mark, °C	+11

The calculations were performed for the conditions of underwater mud volcano “Odesa” of the Ukrainian’s sector of the Black Sea [30]. The composition of the emitting gas [30] is also taken from Table 1. The other initial data are presented in Table 2 (these data have been taken from [13], [30], [32]). The pipeline dimensions assumed to be equal: diameter is 114 mm, wall thickness is 12 mm, length is 2000 m.

As mentioned above Aspen Hysys computer package has been used to perform calculations based on schematic diagram showed in Figure 2. The following parts were used within calculations:

- a) assembly device of a mud volcano;
- b) fluid pipeline;
- c) sea bed gas hydrate deposits.

A collection device of the mud volcano was presented by modeling a mixture of volcanic gas and water flows. The fluid pipeline was filled with water and gas mixture (composition is presented in Table 1) Sea bed gas hydrate deposits were presented in the form of a heat exchanger with heat energy exchange necessary for the dissociation of the deposits.

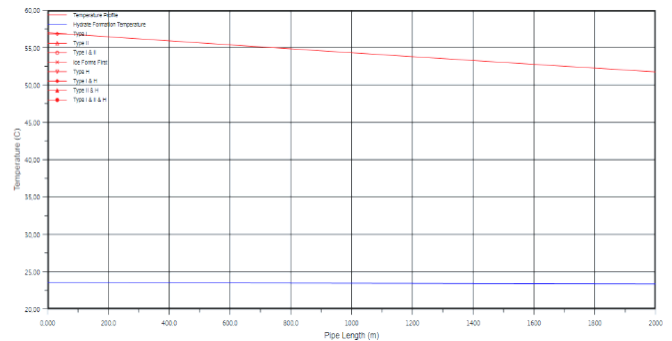
**Table 3. The results of calculations of the flow rate of methane extracted from deposits of gas hydrate using the fluid from the underwater volcano “Odesa” (pipeline has a diameter of 114 mm with an insulating coating with thickness of 10 mm)**

Type of insulation and type of environment of the pipeline	Effective length of the fluid pipeline, km	Volcanic fluid pressure on the hydrate deposit, MPa	The magnitude of the pressure drop, MPa	Temperature at the outlet of the fluid pipeline, °C	The magnitude of the temperature drop, °C	The temperature of hydrate formation at 2000 m, °C	The amount of heat used by fluid, kJ/h	Gas flow from hydrates, m <sup>3</sup> /h	Temperature pressure, °C
Polyurethane (in water)	24.7	24.149	0.849	53.25	3.75	23.36	3.325·10 <sup>6</sup>	2829	42.3
Bitumen (in water)	2.4	24.64*	0.36*	23.18*	33.82*	23.47*	2.357·10 <sup>6</sup> *	2006*	12.2*
Polystyrene (in water)	17.7	24.150	0.85	51.76	5.24	23.36	3.292·10 <sup>6</sup>	2802	41.8
Polystyrene (in sea bed clay)	29.7	24.150	0.85	53.88	3.12	23.36	3.053·10 <sup>6</sup>	2598	42.9

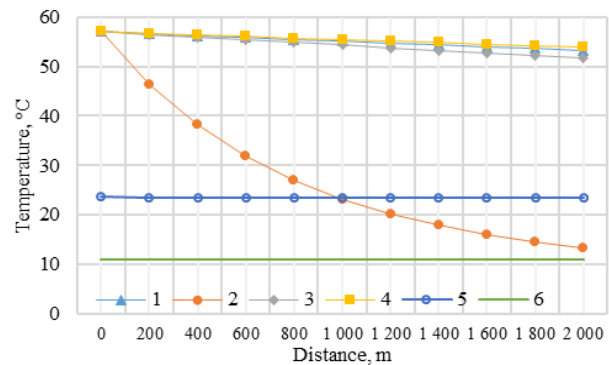
\* Option 2: the data are given for the effective distance of 1000 m between the mud volcano and the hydrate deposit, as under these conditions hydrates are started to form from volcanic fluid inside pipeline

### 3. Results and discussion

The results of the modeling of operating of the fluid pipeline, which directs energy from the mud volcano “Odesa” to the hydrate deposit, are shown in Table 3. Figure 3 shows the results in the form of a screenshot in and Figure 4 shows the results in the form of a graph.



**Figure 3. A screenshot made from calculations by the ASPEN HYSYS computer package for distribution of the actual temperature of the fluid and the equilibrium temperature of hydrate formation when the fluid moves along a pipeline from the mud volcano “Odesa” (pipeline diameter is 114 mm, insulated by polystyrene with thickness of 10 mm; the pipeline is situated at the sea bed)**



**Figure 4. The temperature distribution of the volcanic fluid along the distance and the equilibrium melting temperature of the gas hydrate deposit: 1 – pipeline in water with urethane insulation; 2 – pipeline in water with asphalt insulation; 3 – pipeline in water with polystyrene insulation; 4 – pipeline in wet clay with polystyrene insulation; 5 – the temperature of hydration of volcanic gas in the pipeline; 6 – the melting temperature of the sea bed gas hydrate**

The results presented in Table 3 show, that for the considered conditions, the effective length of the pipeline  $L_{ef}$ , significantly depends on the type of heat-insulation, as the type of insulation determines thermodynamic parameters favourable for hydrates formation inside pipeline. The limit length are:

- 1)  $L_{ef} \approx 24 \cdot 10^3$  m for polyurethane and polystyrene insulation;
- 2)  $L_{ef} \approx 2.4 \cdot 10^3$  m for bituminous.

The amount of heat, which can transferred for the decomposition of hydrates are:

- 1)  $h \approx 3.3 \cdot 10^6$  kJ/h for the pipeline with length of  $2 \cdot 10^3$  m;
- 2)  $h \approx 2.4 \cdot 10^6$  kJ/h for the pipeline with length of  $1 \cdot 10^3$  m.

Also, as can be seen from Figure 3 and 4, the average temperature difference for heat exchange between volcanic fluid and hydrates for the conditions discussed are for:

- 1) 42.3°C with methane flow rate of  $2.8 \cdot 10^3$  m<sup>3</sup>/h;
- 2) 12.2°C methane flow rate of  $2.0 \cdot 10^3$  m<sup>3</sup>/h.

However, it should be noted that the flow of mixture of volcanic fluid and release from gas hydrates methane may make thermodynamic conditions favourable for the formation new hydrates, which will reduce methane debit. Such case may occur due to reduction of water mineralization within the area of pore formation, for example. The reason for this will be mix of this water with fresh water released during melting of gas hydrates at places near mud volcanoes. To calculate the amount of new formed hydrates can be used a stochastic model of the kinetic processes of formation gas hydrates [33]. Also, flow rate of methane from gas hydrates will be reduced by about 10% if pipeline will be lay on the sea bed in comparison with pipeline laying in water (Table 3).

The potential efficiency of the alternative method of methane extraction from gas hydrate sea bed deposits using emissions (fluids) from underwater mud volcanoes can be considered proven based on presented above results of calculations. Additionally, the presented method can be used for extracting methane from gas emissions mud volcanoes themselves, since a significant part of their emissions is methane. Such extraction will reduce pollution of sea and ocean waters by dissolved gases and, as a result, increase a biopotential and a biodiversity of these water areas. Such development meets the requirements of “constructive hydro-ecology” [34].

If the hypothesis of abiogenic origin of subaquatic natural gas is confirmed [35], the resource of this gas and emissions of mud volcanoes (fluids) can be considered as renewable and ecological source of energy sold in the considered alternative method of methane production from sea bed gas deposits.

#### 4. Conclusions

The geological and thermodynamic preconditions for methane production from subaquatic deposits of gas hydrates through the use of emissions (fluids) of mud volcanoes are analysed. It is shown, that such conditions exist in some sectors of the Black Sea.

The circuit-technological solution of the alternative method of methane extraction from gas hydrate deposits by using the emission energy of mud volcanoes (fluids) is considered. The method of calculating potential of an underwater mud volcano as a source of energy for derivation of sea bed hydrates is proposed.

Based on the Aspen Hysys computer package, the mode of operation of the pipeline supplying fluid from the mud volcano to the hydrate deposit was modelled. It was shown the possibility of using those emissions for extracting me-

thane from the active Black Sea mud volcano “Odesa” as an example. The distance to which a flow of mud volcano emissions can be delivered with a temperature sufficient to remove sea bed hydrates from thermodynamic equilibrium and release methane is determined. It was shown that using fluid flow rate of 29.2 thousand m<sup>3</sup>/h and the length of the fluid pipeline  $L = 2000$  m the about 2.0-2.5 thousand m<sup>3</sup>/h methane can be extracted from deposits of subaquatic hydrates.

The obtained results allow us to consider the potential viability of an alternative method of methane production from sea bed gas hydrate deposits under the considered conditions of using the emissions (fluids) of underwater mud volcanoes.

The presented method should be considered as a synergistic one, which allows increase an amount of methane obtained from subaquatic sources for use. It will also prevent methane emissions into the atmosphere, reducing pollution of sea and ocean waters with dissolved gases.

It is possible to use the energy of the gas flow extracted from the subsurface deposits for decomposition of hydrates in the case that hydrate deposits cover subsurface deposits of natural gas with an impermeable layer. This process will be similar to the considered method of using mud volcano emissions.

Further research should be focused on the issues of an effective and environmentally safe process of preparing the flow of emissions of underwater volcanoes for feeding into pipelines, as well as collecting and preparing the flow of gas obtained for further use.

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#### References

- [1] Makogon, Y., Holditch, S., & Makogon, T. (2007). Natural gas hydrates – A potential energy source for the 21<sup>st</sup> Century. *Journal of Petroleum Science and Engineering*, 56(1-3), 14-31. <https://doi.org/10.1016/j.petrol.2005.10.009>
- [2] Koltun, P., & Klymenko, V. (2016). Methane hydrates – Australian perspective. *Mining of Mineral Deposits*, 10(4), 11-18. <https://doi.org/10.15407/mining10.04.011>
- [3] Kvamme, B., Kuznetsova, T., Sapate, A., & Qorbani, K. (2016). Thermodynamic implications of adding N<sub>2</sub> to CO<sub>2</sub> for production of CH<sub>4</sub> from hydrates. *Journal of Natural Gas Science and Engineering*, (35), 1594-1608. <https://doi.org/10.1016/j.jngse.2016.03.095>
- [4] Archer, D., Buffett, B., & Brovkin, V. (2009). Ocean methane hydrates as a slow tipping point in the global carbon cycle. *Proceedings of the National Academy of Sciences*, 106(49), 20596-20601. <https://doi.org/10.1073/pnas.0800885105>
- [5] Ovetska, O., Ovetskyi, S., & Vytyaz, O. (2021). Conceptual principles of project management for development of hydrate and other unconventional gas fields as a component of energy security of Ukraine. *E3S Web of Conferences*, (230), 01021. <https://doi.org/10.1051/e3sconf/202123001021>

- [6] Oveckiy, S., & Savchuk, V. (2016). A method developed to increase technological and ecological efficiency of gas production from hydrate deposits. *Eastern-European Journal of Enterprise Technologies*, 3(10(81)), 41-47. <https://doi.org/10.15587/1729-4061.2016.72545>
- [7] Bondarenko, V.I., & Sai, K.S. (2018). Process pattern of heterogeneous gas hydrate deposits dissociation. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu*, (2), 21-28. <https://doi.org/10.29202/nvngu.2018-2/4>
- [8] Denysov, Yu.P., & Klymenko, V.V. (2014). Sravnitel'nyy analiz tekhnologii dobychi gazogidratnoho metana. *Scientific journal "Geology. Mining. Oil and gas business. Energy"*, 1(3), 13-22.
- [9] Bondarenko, V., Sai, K., Ganushevych, K., & Ovchynnikov, M. (2015). The results of gas hydrates process research in porous media. *New Developments in Mining Engineering 2015: Theoretical and Practical Solutions of Mineral Resources Mining*, 123-127. <https://doi.org/10.1201/b19901-23>
- [10] Wu, N., Zhang, H., Yang, S., Zhang, G., Liang, J., Lu, J., Su, X., Schultheiss, P., Holland, M., & Zhu, Y. (2011). Gas hydrate system of Shenhu Area, Northern South China Sea: Geochemical results. *Journal of Geological Research*, (2011), 1-10. <https://doi.org/10.1155/2011/370298>
- [11] Bi, Y., Chen, J., & Miao, Z. (2016). Thermodynamic optimization for dissociation process of gas hydrates. *Energy*, (106), 270-276. <https://doi.org/10.1016/j.energy.2016.03.029>
- [12] Chong, Z.R., Yang, S.H.B., Babu, P., Linga, P., & Li, X.-S. (2016). Review of natural gas hydrates as an energy resource: Prospects and challenges. *Applied Energy*, (162), 1633-1652. <https://doi.org/10.1016/j.apenergy.2014.12.061>
- [13] Shnyukov, Ye.F., Kobolev, V.P., & Pasynkov, A.A. (2013). *Gazovyy vulkanizm Chernogo morya*. Kyiv, Ukraina: Logos, 383 p.
- [14] Uddin, M., Wright, F., Dallimore, S., & Coombe, D. (2014). Seismic correlated Mallik 3D gas hydrate distribution: Effect of geomechanics in non-homogeneous hydrate dissociation by depressurization. *Journal of Natural Gas Science and Engineering*, (20), 250-270. <https://doi.org/10.1016/j.jngse.2014.07.002>
- [15] da Rosa, A. (2013). Ocean thermal energy converters. *Fundamentals of Renewable Energy Processes*, 137-147. <https://doi.org/10.1016/b978-0-12-397219-4.00004-7>
- [16] *Ocean thermal energy conversion*. (2021). Retrieved from: [https://en.wikipedia.org/wiki/Ocean\\_thermal\\_energy\\_conversion](https://en.wikipedia.org/wiki/Ocean_thermal_energy_conversion)
- [17] Avery, W.H., & Wu, C. (1994). *Renewable energy from the ocean: A guide to OTEC*. New York, United States: Oxford University Press.
- [18] Klymenko, V., Denysov, Y., Skrypnik, O., Kononchuk, S., & Teliuta, R. (2021). Mining of methane from deposits subaquatic gas hydrates using OTEC. *E3S Web of Conferences*, (230), 01009. <https://doi.org/10.1051/e3sconf/202123001009>
- [19] Bondarenko, V., Sai, K., Prokopenko, K., & Zhuravlov, D. (2018). Thermodynamic and geomechanical processes research in the development of gas hydrate deposits in the conditions of the Black Sea. *Mining of Mineral Deposits*, 12(2), 104-115. <https://doi.org/10.15407/mining12.02.104>
- [20] Klymenko, V.V., Vytyaz, O.Yu., & Oveckiy, S.O. (2016). Pro metod vydobuvannya metanu z donnykh hazohidratnykh pokladiv z vykorystanniam vyklydiv pidvodnykh vulkaniv. *Hazohidratni Tekhnologii u Hirnyctstvi, Naftohazoviyi Spravi, Heotekhnitsi ta Enerhetytsi*, 8-9.
- [21] Kessler, J.D., Reeburgh, W.S., Southon, J., Seifert, R., Michaelis, W., & Tyler, S.C. (2006). Basin-wide estimates of the input of methane from seeps and clathrates to the Black Sea. *Earth and Planetary Science Letters*, 243(3-4), 366-375. <https://doi.org/10.1016/j.epsl.2006.01.006>
- [22] Greinert, J., Artemov, Y., Egorov, V., Debatist, M., & McGinnis, D. (2006). 1300-m-high rising bubbles from mud volcanoes at 2080 m in the Black Sea: Hydroacoustic characteristics and temporal variability. *Earth and Planetary Science Letters*, 244(1-2), 1-15. <https://doi.org/10.1016/j.epsl.2006.02.011>
- [23] Cook, J. (2022). *Asphalt\_volcano 2*. Woods Hole Oceanographic Institution. Retrieved from: [https://upload.wikimedia.org/wikipedia/commons/e/ec/Asphalt\\_volcano2\\_h.jpg](https://upload.wikimedia.org/wikipedia/commons/e/ec/Asphalt_volcano2_h.jpg)
- [24] Shnyukov, Ye., & Kobolev, V. (2018). Gas hydrate deposits of methane in the mud volcanoes of the Black Sea. *Geology and Mineral Resources of World Ocean*, (1), 5-34. <https://doi.org/10.15407/gpimo2018.01.005>
- [25] Kudrin, I.V., Kudrin, K.I., & Orlyankin, V.M. (2013). *Sposob dobychi gazov i presnoy vody iz podvodnykh gazogidratov snizheniyem gidrostaticheskogo davleniya*. Patent No. 2402674. Russian Federation.
- [26] Ng, H.-J., & Robinson, D.B. (1985). Hydrate formation in systems containing methane, ethane, propane, carbon dioxide or hydrogen sulfide in the presence of methanol. *Fluid Phase Equilibria*, 21(1-2), 145-155. [https://doi.org/10.1016/0378-3812\(85\)90065-2](https://doi.org/10.1016/0378-3812(85)90065-2)
- [27] Bondarev, E.A., Babe, G.D., & Groysman, A.G. (1976). *Mekhanika obrazovaniya gidratov v gazovykh potokakh*. Moskva, Rossiya: Nauka (Sibirskoye otdeleniye), 158 s.
- [28] Degtyarev, B.V., & Bukhgalter, E.B. (1976). *Bor'ba s gidratami pri ekspluatatsii gazovykh skvazhin v severnykh rayonakh*. Moskva, Rossiya: Nedra, 198 s.
- [29] Makogon, Yu.F. (1974). *Gidraty prirodnykh gazov*. Moskva, Rossiya: Nedra, 208 s.
- [30] Artemov, Yu.G., Egorov, V.N., Gulin, S.B., & Polikarpov, G.G. (2013). New channels for bubble stream discharge of methane in the Sorokin Trough, the Deepwater Black Sea. *Marine Ecological Journal*, 12(4), 27-36.
- [31] Shnyukov, E.F., & Kobolev, V.P. (2018). Gas hydrate deposits in Black Sea mud volcanoes. *Actual Problems of Oil and Gas*. <https://doi.org/10.29222/ipng.2018-5712.2018-23.art70>
- [32] Naudts, L., De Batist, M., Greinert, J., & Artemov, Yu.G. (2009). Geo- and hydro-acoustic manifestations of shallow gas and gas seeps in the Dnepr paleo-delta, northwestern Black Sea. *The Leading Edge*, 28(9), 1030-1040. <https://doi.org/10.1190/1.3236372>
- [33] Klymenko, V., Gutsul, V., Bondarenko, V., Martynenko, V., & Stets, P. (2019). Modeling of the kinetics of the gas hydrates formation on the basis of a stochastic approach. *Solid State Phenomena*, (291), 98-109. <https://doi.org/10.4028/www.scientific.net/SSP.291.98>
- [34] Mandryk, O., Arkhypova, L.M., Pukish, A.V., Zelmanovych, A., & Yakovlyuk, Kh. (2017). Theoretical and methodological foundations of sustainable development of geosystems. *IOP Conference Series: Materials Science and Engineering*, (200), 012018. <https://doi.org/10.1088/1757-899X/200/1/012018>
- [35] Lukin, A.Ye. (2015). Sistema "superplyum – glubokozalegayushchie segmenty neftegazonosnykh basseynov" – neishchepayemyy istochnik uglevododorodov. *Heolohichnyi Zhurnal*, (2), 7-20.

## Альтернативний спосіб видобування метану з покладів субаквальних газогідратів

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**Мета.** Визначення потенційної працездатності альтернативного способу видобування метану з покладів субаквальних газогідратів при використанні викидів підводних грязьових вулканів у геологічних та термодинамічних умовах, характерних для Чорного моря.

**Методика.** Комп'ютерне моделювання процесів зміни термодинамічних параметрів флюїду у трубопроводі, яким він подається до гідратних покладів, здійснено на базі програми Aspen Hysys, із використанням для розрахунку енергетичного потенціалу флюїду моделі Нг і Робінсона.

**Результати.** Розроблено алгоритм розрахунку відстані, на яку може бути доставлено потік викидів грязьового вулкану з температурою, достатньою для виведення донних гідратів з термодинамічної рівноваги і виділення метану. Адаптовано схемно-технологічне рішення альтернативного способу видобування метану з газогідратних покладів шляхом використання енергії викидів грязьових вулканів (флюїдів) в частині: збірний пристрій на грязьовому вулкані – трубопровід флюїду – газогідратні донні поклади, до моделі, яка дозволила для розрахунків використати програму Aspen Hysys.

**Наукова новизна.** Обґрунтовано потенційну працездатність альтернативного способу видобування метану з газогідратних донних покладів в умовах використання викидів (флюїдів) підводних грязьових вулканів. У випадку, коли гідратні поклади покривають непроникним шаром піддонні поклади природного газу, для розкладення гідратів можна використати теплову енергію потоку газу, що видобуватиметься з піддонних покладів, аналогічно розглянутому альтернативному способу використання викидів грязьових вулканів.

**Практична значимість.** Застосування альтернативного способу видобування метану з газогідратних донних покладів шляхом використання викидів грязьових вулканів дозволить в цілому збільшити кількість газу, отриманого з субаквальних джерел, приблизно на 7-10% без використання додаткових інших джерел теплоти. Практичне застосування такого способу також запобігатиме викидам метану з грязьових вулканів в атмосферу, зменшить забруднення вод морів та океану розчиненими газами.

**Ключові слова:** метан, поклади субаквальних газогідратів, підводні грязьові вулкани, флюїди, підводні трубопроводи, термодинамічні параметри флюїду