METHANE GAS HYDRATES OF THE BLACK SEA – ENVIRONMENTAL PROBLEM OR ENERGY SOURCE?

Oleksandr Nalyvaiko
O. M. Beketov Kharkiv National University, Ukraine
ORCID: https://orcid.org/0000-0001-5513-9868

Pavlo Pysarenko
Poltava State Agrarian University, Ukraine
ORCID: https://orcid.org/0000-0002-4915-265X

Yevhenii Nalyvaiko
Poltava State Agrarian University, Ukraine
ORCID: https://orcid.org/0000-0002-7597-8762

Nikolay Tanchev
Ecological fund Geya, Bulgaria
ORCID: https://orcid.org/0000-0001-6644-7903


Purpose. The purpose of this paper is to substantiate the technological solution of equilibrium conditions in the system “methane – water phase – hydrate – R-2M”; to reveal existing ecological problems of methane gas hydrate extraction from the Black Sea bottom; to determine whether gas hydrate deposits of Black Sea methane are an ecological problem or should be considered as an energy source, to explain the necessity of introduction of the effect of forced self-preservation of methane gas hydrates into development of gas hydrates from the sea bottom.

Results. This article analyses current research on gas hydrates specifically in the Black Sea. It shows that the necessary conditions exist for the accumulation of gas hydrates in certain areas of the deep Black Sea (one of the most favourable regions among modern sea basins). This article discusses some ideas for the development of experimental studies of the metastable state of methane gas hydrates at negative temperatures: stability and mechanisms of decomposition. Despite the great variety of technological solutions and schemes of gas hydrates application proposed by the leading researchers in the world, they have been tested practically on a small number of laboratory and model installations, mainly for water desalination and concentration of water solutions, separation of two-component gas mixtures. In fact, there is no data to calculate the processes of formation and melting of ice-gas hydrate methane. The effect of self-preservation of methane gas hydrates deserves special attention.

Scientific novelty. An attempt was made to substantiate the issue of whether gas hydrate deposits of methane in the Black Sea are an environmental problem or should they be considered as an additional source of energy and even as a “fuel of the future”. The authors for the first time introduced the concept of “forced preservation (activation) effect of methane gas hydrates”, which makes it possible to stabilize methane hydrate decomposition when the system is transferred from the area of hydrate stability to the area of thermodynamic parameters, thus significantly reducing the environmental problems of the Black Sea.
Practical value. This article offers a technological solution for stabilization of equilibrium conditions by hydrophobic material “Ramsinks-2M” in the system “methane-water phase-hydrate-R-2M” to regulate the self-preservation effect of methane gas hydrates.

Key words: gas hydrate, metastable state, methane, kinetics and thermodynamics of processes, melting, heat exchange, thermal conductivity, phase equilibria, innovation.

Introduction. The interest of scientists in gas hydrates is mainly due to the existence of methane hydrates in nature in quantities comparable to proven conventional gas reserves, their high energy content and their global environmental significance. The tendency of continuing depletion of the world conventional hydrocarbon reserves is more urgent today than ever for Bulgaria and the EU countries. Therefore, the problem of further study of the resource potential of methane hydrates and their use for natural gas production is being studied in many countries. In general chemistry, gas hydrates are called clathrates.

Natural gas hydrates are the only undeveloped source of natural gas on Earth that, thanks to their vast resources and widespread distribution in the near future, when environmentally friendly methane gas hydrate extraction and transportation technologies are created, could really compete with conventional deposits. Gas hydrates are metastable formations. Changes in temperature and pressure can cause them to decompose, releasing methane and water (1 m$^3$ of gas hydrate contains 0.2 m$^3$ of gas and 0.8 m$^3$ of water), which provokes underwater collapses and large-scale landslides and leads to serious geo-environmental problems.

Methane is a so-called greenhouse gas and its extraction would make it possible to reduce emissions into the atmosphere by several times (up to 200 cubic meters of methane would be obtained from one cubic meter of “warm ice”). Thus, the exploitation of hydrate gas deposits solves a double problem: the possibility to significantly improve the existing environmental problem of the Black Sea and to obtain methane hydrate gas as a new source of energy.

The use of non-conventional energy sources from the sea has become a pressing and, moreover, not only theoretical but also practical issue for the countries of the Black Sea area. Methane gas hydrates, a solid condensate of natural gas, are of serious interest. This substance is stable only at low temperatures and at pressures above 40 atmospheres. If raised to the surface, the solid condensate will melt quickly, releasing methane. For the Black Sea, the gas hydrate stability zone starts at a depth of 500–900 m and has an average thickness below the bottom of 300 m.

The research carried out within the SUGAR project by the German ship “Maria S. Merian” proves that gas hydrates are abundant not only in the Black Sea in general, but also specifically off the Bulgarian coast [1]. Seismic and electrical 2D and 3D surveys, heat flow measurements and geochemical testing were carried out. The final results of the expedition will be announced by the team of the German project SUGAR, which carried out the research.

Although the Institute of Oceanology of the Bulgarian Academy of Sciences has been developing a multi-parameter model to study gas hydrates since 2000,
there is still no clear estimate based on the available data; it is difficult to say exactly what the gas hydrate methane reserves of the Black Sea basin are. Two possible models, an optimistic and a pessimistic model, were proposed to study the estimation of gas hydrate reserves in the Black Sea basin. According to the optimistic model, the area of the gas hydrate stability zone in the Black Sea is 280,000 sq. km while according to the pessimistic model the area of gas hydrate stability zone is 290,000 sq. km.

Potential deposit of gas hydrates in the Bulgarian CH₄: in GH 3,400 billion m³) + 132 billion m³ of free gas, estimated resources (based on seismic and geothermal research). Hydrates are stable at high pressures and low temperatures. They exist at depths >400 m and in sediments under the sea bottom 0 m – 600 m D m G.

Conceptual extraction technologies:
- Pressure reduction;
- Layer heating;
- Inhibitor injection;
- Chemical exchange – replacement with CO₂.

Motivation for European policymakers. Natural gas from local (European) gas hydrates deposits should play an important role in the future European energy system in order to:
- Increase the security of European energy supply;
- Help to reduce CO₂ emissions by replacing coal as an energy source;
- In addition to renewable energy sources and stabilization of the energy system by feeding power generation systems during periods of low wind and/or low electricity. Briefly: gas hydrates can replace conventional gas reserves in Europe, which will be depleted in the coming decades, and reduce Europe growing dependence on imported natural gas.

Required action:
- Study and assessment of the European (and national for Bulgaria) energy resources of sea gas hydrates and consideration of the identified deposits as reserve energy sources for use in emergency situations;
- Development of national programmes for exploitation of the energy resources of sea gas hydrates through active cooperation with leading European countries in the field of development of technologies for exploration and extraction of natural gas from gas hydrates;
- Training of own marine specialists for exploration and production of methane from gas hydrates [2].

The Black Sea will be the subject of more intensive research in the coming years due to the high prospects of its bottom in terms of both hydrate and oil and gas content. It should be noted that the results of studies on the extent of hydrate-bearing sedimentary sections of water areas, besides the applied resource potential of hydrate and sub-hydrate deposits, are also of great importance for the development of several countries, including Bulgaria.
The introduction of new science-intensive technologies allowing to solve the problems of energy resources and ecology, effective use of unconventional energy sources and raw materials on a qualitatively new level is essential for Ukraine and Bulgaria. A new scientific direction – development and use of gas hydrate technologies is promising in solving these issues.

The relevance of the work is related to the fact that methane gas hydrates can become a reliable and long-term source of natural gas, especially for countries that are experiencing an acute shortage of energy resources. Gas hydrate technologies, compared to existing ones, allow to transport natural gas with greater energy efficiency, to separate mixtures of gases and liquids, to compress gases to high pressures, to concentrate water solutions, to extract and accumulate cold, to utilize and store CO₂, etc. Their study is also important for solving the problems of developing methane gas hydrate deposits in the Black Sea.

Gas hydrates are supramolecular crystalline compounds of clathrate type in which molecules of non-polar or low-polar substances are “included” in the ice-like structure of water and held by van der Waals forces. Such compounds are capable to form most gases and their mixtures as well as some organic liquids.

Despite the great variety of technological solutions and schemes of gas hydrates application proposed by the leading researchers in the world, they have been tested practically on a small number of laboratory and model installations, mainly for water desalination and concentration of water solutions, separation of two-component gas mixtures. In fact, there is no data to calculate the processes of formation and melting of ice-gas hydrate methane. The effect of self-preservation of methane gas hydrates deserves special attention.

The generation, migration and accumulation of hydrocarbons is a fundamental problem of petroleum geology. All known gases can exist in a wide range of pressures and temperatures, forming crystalline hydrates at certain pressures and temperatures, the structure of which depends on gas composition, pressure and temperature. The known development methods focus on lowering reservoir pressure below the equilibrium pressure, raising the hydrate temperature in the reservoir above the equilibrium temperature and injecting decomposition catalysts and their combination into the reservoir. They suggest that a specific feature of developing gas hydrate deposits is the need to convert their gas in the reservoir from a solid state to a free state, with further extraction using conventional technologies. The field development of methane gas hydrates from the bottom of the Black Sea has not actually started, primarily due to the lack of environmentally safe methods and technologies for their exploitation.

Most modern scientists assess the Black Sea as a promising area for prospecting and exploring gas hydrate deposits on an industrial scale. This article offers a technological solution for stabilization of equilibrium conditions by hydrophobic material “Ramsinks-2M” in the system “methane-water phase-hydrate-R-2M” to regulate the self-preservation effect of methane gas hydrates [4; 5].
**Review of literature.** Analysis of the scientific references indicates that the influence of methane gas hydrate preservation on the bottom of the Black Sea is an essential condition for the development of gas hydrate deposits. There is a significant number of scientific studies on the mechanism of formation of methane gas hydrate deposits, in particular, on the bottom of the Black Sea.

The most significant of them are works of I. Butovski [1], S. Byk et al. [2], V. Bondarenko et al. [3], Yu. Denysov et al. [4], S. Hoshovskyi, A. Zurian [5], R. Dychkovskyi et al. [6], P. Englezos [7], A. Nesterov [8], V. Klymenko et al. [9–11], O. Nalyvaiko et al. [12–13], V. Yakushev et al. [14], J. Rajnauth et al. [15] K. Wallmann et al. [16] and other researchers.

It should be emphasized separately that research scientists [15] and other specialists devoted their scientific works to the development of the theoretical foundations of the formation of gas hydrates. In this article, we reveal the mechanism of influence of the “Ramsinks-2M” additive in experimental studies of the formation of gas hydrates in the “H2O(ice)-CO2(gas)” system.

Gas hydrates are crystalline compounds formed from water and gas under certain thermobaric conditions with low molecular weight. The physical and chemical properties of gas hydrates, the possibility of their formation, storage and dissociation in a quite wide and convenient for practical application range of pressures and temperatures allows for more efficient separation of gas and liquid mixtures, concentration and separation of water solutions, gas compression to high pressures, production and accumulation of cold, etc. compared to existing technologies.

However, today all scientific studies on the mechanism of self-preservation or preservation of gas hydrates in the Black Sea, their transportation and storage are purely theoretical, i.e. they are hypotheses requiring huge financial outlays with an unknown end result. At best, the formation of gas hydrates is being studied under the laboratory conditions.

The approach to the extraction and transportation of gas hydrates discussed in the article is the first practical step in the development of gas hydrate deposits (technical specifications of the industrial plant and technological regulations for obtaining water repellent formulation with a hydrophobic element “Ramsinks-2M” were approved, experiments to study changes in the thermobaric conditions of gas hydrates using the estimated amount of “Ramsinks-2M” were successfully carried out, etc. In our opinion, this approach is innovative.

**Materials and methods.** The purpose of this paper is to substantiate the technological solution of equilibrium conditions in the system “methane – water phase – hydrate – R-2M”; to reveal existing ecological problems of methane gas hydrate extraction from the Black Sea bottom; to determine whether gas hydrate deposits of Black Sea methane are an ecological problem or should be considered as an energy source, to explain the necessity of introduction of the effect of forced self-preservation of methane gas hydrates into development of gas hydrates from the sea
Gas hydrates are solid crystalline compounds of the M-nH₂O type, in which a low molecular weight hydrophobic gas with a molecular weight M is held inside n water molecules by hydrogen bonds under certain thermobaric conditions: temperature below the first tens of degrees and pressure up to 40 MPa. The authors of the article, taking into account that a low molecular weight hydrophobic gas is present in the structure of methane gas hydrate, conducted a number of experiments in a laboratory facility to study the stabilization conditions of methane gas hydrate behaviour when exposed to the hydrophobic material “Ramsinks-2M” produced by the authors, in order to understand the forced preservation of methane gas hydrate.

This technological solution for the development of gas hydrate methane deposits in the Black Sea is necessary in order to stabilize conditions by regulating the equilibrium in the system “methane-water phase-hydrate-R-2M”, which in turn allows to regulate the process of methane gas hydrate preservation, which the authors called the “effect of forced preservation of methane gas hydrate”. In natural gas hydrates, 98% of gas is represented by methane, 1 m³ of hydrate can contain up to 160 m³ of gas under normal conditions.

**Results and discussion.** The changes in temperature and pressure can cause them to decompose, releasing methane and water (1 m³ of gas hydrate has 0.2 m³ of gas and 0.8 m³ of water), which provokes underwater collapses and large-scale landslides and leads to geo-ecological problems.

The decomposition of hydrates after pressure release begins on their surface and proceeds in several stages: fast and subsequent slow stages can be distinguished, in some cases up to almost complete stop of the decomposition process – self-preservation effect. After the thermodynamic analysis of the surface decomposition of gas hydrates we first consider the surface decomposition of gas hydrates in connection with the process of methane hydrate decomposition. A practically important question arises: how exactly will the decomposition of methane hydrates occur and what is the stage of this process when the system is transferred from the region of hydrate stability to the region of thermodynamic parameters.

As experimental data show, in the area of thermobaric parameters, where the stable phase is hexagonal ice, the decomposition of hydrates may also cause the appearance of intermediate metastable water phases – cubic ice or supercooled water [14]. There are the following theoretical possibilities for the initial stage of the decomposition process when the pressure in the system is released:

a) evaporation (sublimation) of hydrate, i.e. its decomposition into gas and water vapour;

b) decomposition of hydrate into gas and condensed water phase (into ice or supercooled water).

For artificial production of hydrates in industrial facilities, the principle of the flow of one or another phase, i.e. dynamic methods is proposed to apply [1]. This
technological complex consists of a reactor with different types of mixers, systems for supplying gas, water phases and their combined thermostating [2]. A significant disadvantage of processes for production of artificial hydrates of natural gas in reactors of dynamic type is their multistage [4].

Secondly, gas hydrates can also be produced under static conditions [10]. Static conditions of gas hydrates production mean the absence of external mechanical influences on the system [9], and the synthesis process is conditioned only by maintaining the necessary parameters of temperature and pressure in the system [6].

“Ramsinks-2M” is a hydrophobic additive (water repellent) complex organosilicon substance, manufactured according to the special technology [9]. Hydrophobic material “Ramsinks-2M” is produced according to TU 2169-323-5349403 of 2005 based on the patent of Ukraine for the useful model N. 4700 E21B43/22 of 17.01.2005 [12].

Hydrophobic dispersed material “Ramsinks-2M” are particles of finely dispersed white powder, insoluble in water and mostly composed of spherical particles with a diameter of 0.01–0.09 mcm. They have an extremely high surface area of 40–60 m²/g. Their bulk density is 0.09 ... 0.25 g/cm³, humidity during storage in an open container does not exceed 0.05%, the residue on a sieve with a grid N. 0315 does not exceed 0.15%. The material is relatively stable, inert, not sensitive to temperature changes, does not foam and is a soft blocking material.

However, it was not known how “Ramsinks-2M” affects the formation of gas hydrates, so it was necessary to carry out appropriate experimental studies. In the course of the experiment on changing the rate and time of gas hydrates formation in the system “hydrate-forming agent – water”, the determination of the zone of influence of hydrophobic dispersed material “R-2M” was studied.

Using the analysis of the calculated conditions of the multiphase equilibrium state “(water phase + gas phase) – gas hydrate + R-2M” (Table 1) by kinetic considerations, it can be assumed that at the initial stage of methane gas hydrate decomposition, the process of transformation of hydrate crystalline lattice of water hydrate phase into ice crystalline lattice-phase starts (Figure 1).

### Table 1

<table>
<thead>
<tr>
<th>Temperature, below 273 K</th>
<th>Pressure, MPa</th>
<th>Water phase</th>
<th>Gas phase</th>
<th>Hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>230.15</td>
<td>0.0</td>
<td>0.5</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>240.15</td>
<td>0.1</td>
<td>0.6</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>250.15</td>
<td>0.3</td>
<td>0.8</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>255.15</td>
<td>0.5</td>
<td>1.2</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>260.15</td>
<td>1.0</td>
<td>1.6</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>265.15</td>
<td>1.6</td>
<td>2.0</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>270.15</td>
<td>2.5</td>
<td>-</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>273.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Source: [11; 13].
The initial stage of methane hydrate decomposition can proceed through the formation of various intermediate metastable phases, the decomposition mechanisms of which may vary depending on the thermobaric conditions. The temperature limit (endpoint) at this pressure is in the range of 273 K.

Figure 1. Calculated conditions of the three-phase equilibrium “water phase – gas phase – gas hydrate + R-2M” at temperatures below 273 K.

Source: [11; 13].

Therefore, an important role is assigned to the stabilization of methane hydrate with its forced self-preservation by the hydrophobic material “R-2M”, in the three-phase equilibrium conditions “water phase – gas phase – gas hydrate + R-2M” (Table 2).

Table 2

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Pressure, MPa</th>
<th>Water phase</th>
<th>Gas phase</th>
<th>Hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>230.15</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>240.15</td>
<td>0.2</td>
<td>0.6</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>250.15</td>
<td>0.3</td>
<td>0.8</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>255.15</td>
<td>0.5</td>
<td>1.2</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>260.15</td>
<td>1.0</td>
<td>1.6</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>265.15</td>
<td>1.6</td>
<td>2.0</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>270.15</td>
<td>2.5</td>
<td>-</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>273.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Source: [11; 13].

Figure 2 shows the conditions for the possible decomposition of methane hydrate into gas and ice and its forced stabilization when the system is transferred to
methane gas hydrate states “(water phase + gas phase)-gas hydrate + R-2M”.

The hydrophobic material “Ramsinks-2M” has such physical and chemical properties, which allow it to form a separate phase in the system “hydrate-forming agent – water-R-2M” between the gas and the water phase, or to make a film coating of gas hydrate. This mechanism of the hydrophobic material “Ramsinks-2M” causes a change in surface tension between the gas and water phases, which leads to a nearly complete blocking of the formation of the water phase in the system, and thereby increases the capacity properties of the gas phase in the system “hydrate-forming agent – water – R-2M”.

![Diagram](https://is-journal.com)

**Figure 2.** The features of methane hydrate stabilization during its forced self-preservation by hydrophobic material “Ramsinks-2M”: 1 – hydrate in the stable state; 2 – transition area of the possible decomposition of methane hydrate into gas and ice; 3 – area of forced preservation of methane gas hydrate by hydrophobic material “Ramsinks-2M”

*Source: [11; 13].*

The research results suggest the following conclusion: hydrophobic disperse material “Ramsinks-2” penetrating into the pore space of the system “hydrate-forming agent – water – Ramsinks-2” leads to a partial reduction of the water phase of the sample and significantly reduces the rate and time of gas hydrate formation in the system “hydrate-forming agent – water – R-2M”.

The study of hydrate formation conditions is important both for the prevention of gas hydrate formation in oil and gas production and pipeline transport systems and for intensification of gas hydrate formation in various technologies of their application for: non-pipeline transport of natural gas, separation of gas-liquid mixtures, gas compression to high pressure and cold accumulation, CO₂ utilization, etc. [2; 4].

To prevent hydrate formation, substances are used under the term inhibitors,
and to accelerate hydrate formation the term promoters is used [10].

There are substances that under certain conditions are inhibitors of hydrate formation, and under other conditions are promoters of this process, such as methanol, ethanol, micronanopowders of metal oxides. As a rule, experimental studies are needed to find out under what conditions a substance is an inhibitor of gas hydrate formation, and under what conditions it is a promoter.

The preliminary experimental assessment of R-2M influence on gas hydrates formation was carried out by express method in the research laboratory of gas hydrate and thermal cooling facilities of the Central Ukrainian National Technical University. The main element of the experimental setup is a gas hydrate crystallizer made in the form of a cylindrical stainless steel high-pressure vessel of a total volume of 150 cm³ and equipped with viewing windows at the ends. CO₂ was used as a hydroforming gas [13].

A cooling chamber was used for pre-cooling and thermostating of the crystallizer. It was experimentally found that under static conditions (without mixing) time to gas hydrate formation ς in the system “H₂O + CO₂” was 120 min, and in the system “H₂O + CO₂ + R-2M” formation of gas hydrates was not observed.

In the process of mixing, in the system “H₂O + CO₂ + R-2M” the time before gas hydrate formation had a minimum value of ς = 20 min at R-2M concentration equal to 50 ppm, at 100 ppm it reached a value of 45 min and remained so at a concentration of 200 ppm. In the absence of R-2M additives, ς was equal to 60 min. This allows to conclude that under mixing conditions at the mentioned concentrations, additive R-2M acts as a promoter of hydrate formation. This additive probably acts as an inhibitor at higher R-2M concentrations, implying that after reaching a minimum value at 50 ppm, at higher R-2M concentrations: 100 ppm and 200 ppm τ increases. Further experimental research is needed to determine the inhibitory capacity of R-2M under dynamic conditions [11].

At the end it should be noted that when water is removed from the crystallizer, additive R-2M is deposited on the sight glasses in the form of a thin layer (Figure 3).

![Figure 3. View of sight-glass after the experiments with additive “Ramsinks-2M”](source: [11; 13].)
The thickness of this layer is proportional to the size of individual microparticles, and the interaction of adsorbed sediment with the windows surface is characterized by a large value of adhesion forces [12].

So, probably, one should agree with V. Beshkov, who believes that scientists need to move from purely scientific research to the next step – directly offer technologies for industrial application, for example by preparing project applications for the European Horizon 2020 programme in order to secure funding for the experimental-industrial part of research aimed at solving energy issues (sample-experiment-introduction). In fact, this is the ultimate goal of basic applied science, especially in the energy field to increase oil and gas production.

Conclusions. Natural gas hydrates are regarded as a potential source of hydrocarbons, but even small concentrations of gas hydrate in rocks can cause a number of problems during drilling, development, testing, plugging, and operation of wells.

It is a reliable fact that in the development of gas hydrate methane deposits, a number of problems and peculiarities arise which prevent the application of the classical technologies. During the development of technologies for methane extraction from gas hydrate deposits in the Bulgarian economic zone of the Black Sea, it is advisable to preliminary assess the possible environmental problems of application of such technologies at a level of experimental laboratory experiments. Such experimental studies are also appropriate for the technologies to extract hydrogen sulfide from deep water and hydrate deposits. For methane gas hydrate deposits with thermodynamic conditions, the presence of large concentrations of hydrogen sulfide and carbon dioxide in hydrocarbons has a significant impact on hydrate formation. In this regard, a study of the kinetics of natural gas hydrate formation under a wide range of thermobaric conditions simulating reservoir and field conditions is reasonable.

In order to clarify the geolocation and characteristics of the deposits of methane and hydrogen sulfide gas hydrates as well as to determine the possible presence of hydrocarbon deposits under them in the Bulgarian economic zone of the Black Sea, additional geological studies should be carried out. In this connection, it is advisable to study the kinetics of natural gas methane and hydrogen sulfide hydrate formation under a wide range of thermobaric conditions simulating reservoir and field conditions.

The authors for the first time introduced the concept of “forced preservation (activation) effect of methane gas hydrates”, which makes it possible to stabilize methane hydrate decomposition when the system is transferred from the area of hydrate stability to the area of thermodynamic parameters, thus significantly reducing the environmental problems of the Black Sea.

Further field and research experiments to stabilize the equilibrium in the “methane-water phase-hydrate-R-2M” system are required to understand the process of preservation (activation) of methane gas hydrates in the bottomhole (reservoir)
zone, which makes it possible to consider the deposits of methane gas hydrates as an additional energy source and even as a “fuel of the future”.

**References**


