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HAZARDS OF UNCONTROLLED METHANE RELEASE FROM CLATHRATES ANALYSE AND ENVIRONMENTAL EVALUATION OF EXTRACTION METHODS

Uncontrolled methane release from clathrates may intensify global warming, causes deoxygenation and changes of pH of oceanic water, prompt tsunami and other hazards. On the other hand, it can be a great source of unconventional fossil fuels in the future, when conventional sources will be depleted and renewable sources not enough developed. The problem is how to ensure its safe exploitation. Methane clathrate breakdown, environmental impacts and feedback between them are presented and possible commercial methods of methane exploitation are compared. Finally, a selected method of methane clathrate exploitation that minimalizes environmental hazards is proposed. Among possible methods such as thermal stimulation, depressurization, inhibitor injection and gas exchange, only the latter one is ecologically friendly and can diminish climate warming with simultaneous CO₂ sequestration.

1. INTRODUCTION

Depletion of conventional fossil fuels and relatively slow development of renewable energy sources (petroleum, coal, and natural gas continue to meet over 80% of global primary energy demand) has stimulated in recent years extensive research on the production of energy from alternative, non-conventional resources, which include methane clathrates. Another reason for the interest in CH₄ clathrates is the risk of their destabilization which can intensify global warming and locally cause natural disasters such as tsunamis.

Methane clathrate is an unstable crystalline structure composed of a methane molecule surrounded by a cage-like frame formed by hydrogen-bonded water molecules. Its mass contains approximately 85% of water. Apart from methane, it can also con-

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tain other hydrocarbons (ethane, propane, butane) and carbon dioxide. Since methane in clathrates is generated mainly through the process of anaerobic digestion, it may occur together with hydrogen sulfide and ammonia. Three main crystalline structures of clathrates exist, I, II and H, differing in cage size. The most common water lattice in structure I consists of 46 molecules which capture gas molecules in two small and six large cages. Structures II (composed of 136 water molecules) and – specially – H structure (34 molecules) are rarely formed with methane molecules. The stability of these structures depends on how many gas molecules are captured within the cages. On average, 1 mole of methane is incorporated by 5.75 moles of water and 1 m³ of clathrate structure I contains 168 m³ of gaseous methane at standard temperature and pressure (STP).

According to various estimates, reservoirs of methane clathrate deposits range from 500 to 2500 Pg in terms of carbon [1], that is 5–25 times more than natural gas resources from conventional deposits which are sufficient for about 60 years of production at current levels. Reservoirs of coal are of similar order to the carbon contained in CH₄ clathrates (approximately 1000 Pg) and will be depleted in about 150 years, given the current rates of extraction.

In view of the above facts and the inhibition of nuclear energy development after the Fukushima disaster, the exploitation of methane clathrates seems inevitable. However, it must be preceded by a thorough analysis of the hazards resulting from the risk of destabilizing their deposits. On the other hand, even if methane clathrates are not exploited, they may decompose because of the progressing global warming, and – as a result of positive feedback – they may further accelerate the process of global warming. There is no broader analysis of this issue in professional literature, even though the climate changes caused by the destabilization of clathrates have already been ascertained over the history of the Earth.

Economic exploitation of methane from clathrates should be preceded with a discussion and a thorough evaluation of potential environmental effects. This paper has been intended to take a stance in the debate and to propose technology for capturing methane from clathrates that would best minimize potential hazards for the environment and climate.

2. CONDITIONS FOR METHANE FORMATION AND RELEASE FROM CLATHRATES

Natural formation of clathrates from water and methane occurs when temperature is close to 273 K and the pressure is higher than 3–4 MPa (Fig. 1). Such conditions occur in the bottom sediments of seas and oceans, mainly in the area of continental shelves, and in the Arctic permafrost regions. Over 230 deposits that have been discovered so far are located mainly on the continental slopes of both Americas, off the

coast of Japan, Norway and New Zealand, in the region of the Arabian Sea, as well as in the permafrost areas of North America and Asia [2]. The largest deposits occur along the Blake Ridge off the coast of North Carolina, in the Gulf of Mexico and in the Nankai Trough off the coast of Japan.

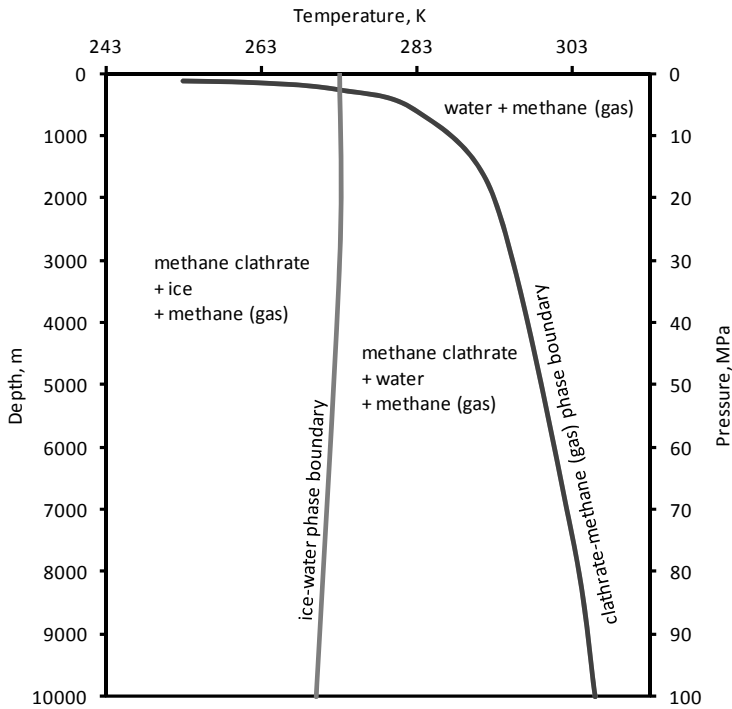


Fig. 1. Approximate phase diagram of methane/water in oceanic bottom sediments – on the base of [3, 4]

Stability zone of methane clathrate extends from the depth of approximately 300 m below sea level to 2000 m below the bottom sediment surface and depends on pressure, temperature, water salinity and the chemical composition of clathrates [5, 6]. Most threatened by increased temperature are clathrates found in shallow waters but the release of methane from them can also destabilize deeper deposits. Disintegration of methane clathrates may also be caused by the pressure decrease, which results from the lowering of sea level, melting of ice sheets on the permafrost areas or exploitation of adjacent natural gas deposits. On the other hand, temperature increase causes melting of glaciers leading to the sea level rise and builds up the pressure against the deposits beneath seafloor. Natural causes for the destabilization of clathrates may also include: tectonic movements, submarine slumps and slides of rocks and sediments, or increased volcanic activity such as occurred, e.g., in the area of the northern Atlantic and the Caribbean in the Cenozoic Era [7].

3. HAZARDS POSED BY BREAKDOWN OF METHANE CLATHRATES

The release of methane from clathrates to the atmosphere is considered to be one of the main reasons for the periodic warming of climate. The relationship between the concentration of methane in the atmosphere (estimated from the research on ice cores) and atmospheric temperature over the last 420 000 years has been noted by Wuebbles and Hayhoe [8]. They connected the synchronic changes in temperature and the concentrations of methane in the glacial and interglacial periods with alternating periods of destabilization and stability of methane clathrate deposits identified on the basis of geological data recording varying participation of individual carbon isotopes in the sediment.

Methane released from below the oceanic bottom sediments is partially oxidized in the aqueous phase both by aerobic and anaerobic microorganisms. Under aerobic conditions, the product of the reaction is CO_2 which decomposes carbonates and lowers the pH of the environment. Under anaerobic conditions, methane is oxidized by sulfate-reducing bacteria, which leads to precipitation of pyrite and carbonates, resulting in pH increase. In an aerobic environment, no anaerobic methane oxidation occurs, even in the presence of large amount of sulfates. It can occur only in the pore space of the sediment, where free oxygen is not available, or when aerobic processes lead to deoxygenation of water – that is anaerobic oxidation follows aerobic oxidation [9]. Deoxygenation of water and bottom sediments leads to a gain in organic deposits. This phenomenon is used to explain the “mass extinction” in the Permian and Triassic periods. According to Heydari and Hassanzadeh [10] what happened then was reduction of the ^{13}C carbon isotope content in marine carbonates and in marine and terrestrial organic matter which could have resulted from a higher proportion of the ^{14}C isotope derived from the released methane. The validity of this hypothesis is also confirmed by Jiang et al. [9], indicating a decrease in pH and widespread oxygen deficiency of oceanic waters, increased precipitation of calcite crystals and reduction of the oxygen content in the atmosphere at that time. On the other hand, the works of Jiang et al. [9, 11] present the hypotheses concerning the formation of carbonate lid covering glacial formations in the late Neoproterozoic, based on the theory of the release of methane from clathrates during deglaciation and the flooding of continental shelves. As a result of the extremely cold climate, the zone of clathrate stability could have reached small depths and their reservoirs at that time were probably the biggest in the history of the Earth. Under these conditions, the release of methane from clathrates as a result of temperature rise took place on a massive scale. Part of the released methane increased the greenhouse effect and, as a result of positive feedback, it led to rapid deglaciation and subsequent destabilization of next deposits. The bottom layer of the carbonate cover in bottom sediments was formed at the end of deglaciation, when oceans were low in oxygen and anaerobic oxidation of methane was prevailing. The

release of methane from clathrates also took place in the Mesozoic Era, when the temperature was relatively high and oceanic waters were generally anoxic.

In the long term, destabilization of methane clathrate deposits results in climate change. In addition, it may also be the cause of local natural disasters such as tsunamis, caused by, e.g. a landslide of underwater sedimentary rocks as a result of the release of methane or tearing off the clathrate-bearing overhangs of deposits from the underwater slope. Descriptions of such events in the history of the Earth were presented, among others, by Paull et al. [12] and Beauchamp [13]. The most well-known example cited by the above mentioned authors is the slide of the rocks off the north-west coast of Norway, near the city of Trondheim, which occurred about 7000 years ago. It is estimated that at that time there was a shift of 5500 km^3 of rocks and bottom sediments at a distance of about 800 km inward the Norwegian Sea. Traces of rapid slides of deposits are also evident in the Blake Ridge area, off the east coast of the United States of America (the offset of approximately 13.4 km^3 of sediment) [14].

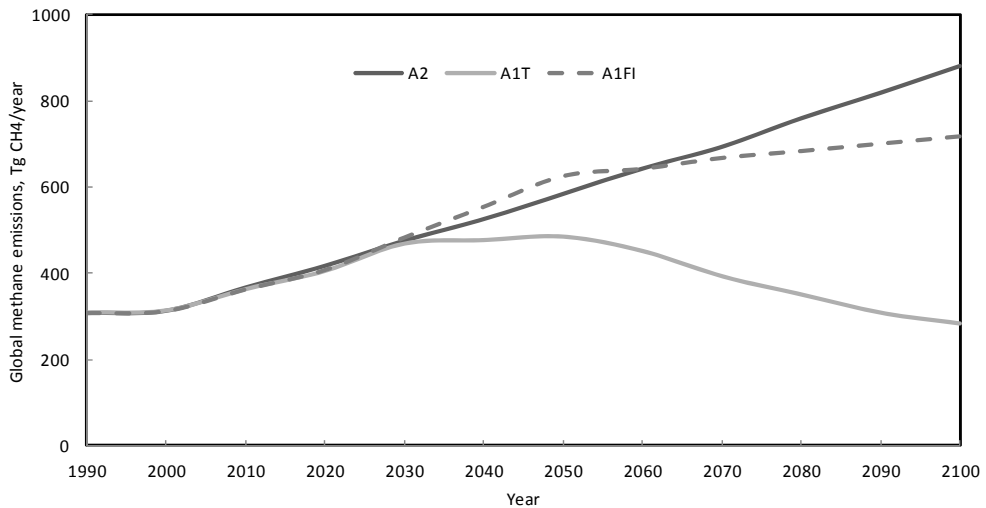


Fig. 2. Global methane emission for selected scenarios
– on the base of IPCC Special Report on Emissions Scenarios (2000)

Hence, in addition to natural causes, the risk of uncontrolled release of methane from clathrates may in future be also associated with their careless exploitation. This thesis is confirmed by *the IPCC Special Report on Emissions Scenarios* (2000). It contains estimates of greenhouse gas emissions and their potential effects on climate. Two groups of scenarios (A1 and A2) assume exploitation of the deposits of methane clathrates. Figure 2 shows the A1 family of scenarios divided into subset A1FI, which is characterized by intensive use of fossil fuels, and A1T, which was founded for the intensive development of solar and nuclear energy. A scenario assuming, among oth-

ers, deriving energy from oil and gas, as well as from unconventional sources, containing methane clathrates, is included in the subset A1FI together with a scenario assuming generation of energy mainly from coal. Projected global methane emission is the biggest in scenarios A2 and A1FI, which involve exploitation of methane clathrate deposits.

In spite of more frequent observations of the release of methane from currently occurring clathrate deposits (e.g., in the Svalbard archipelago in the region of Spitsbergen, in the vicinity of New Zealand [7] and on the East Siberian Arctic Shelf [15]) no studies address how much its current release is influenced by the progressing climate change. Professional literature presents only the estimates of methane releases, which were examined, among others, by Kroeger et al. [7] as well as Shakhova and Semiletov [16]. These quantities can reach tens of Tg CH₄/yr. Some prospects for extending knowledge in this field are offered by PERGAMON, the project commenced by the European Commission in 2009 aiming to coordinate research on methane release in the Arctic and its monitoring.

4. TECHNOLOGIES OF METHANE EXTRACTION FROM CLATHRATES

Basically, there are four known technologies of cost-effective exploitation of methane clathrate deposits and their combinations: thermal stimulation, depressurization, inhibitor injection and the gas replacement of methane with carbon dioxide.

The method of thermal stimulation means the providing of heat influx to the deposit via hot liquid or steam, with the use of electric or shortwave heating, or by initiating a process of controlled combustion of fuel supplied together with the air into the combustion chamber placed within the deposit. The simplest system assumes using two or three wellbores – one is used to introduce a heating medium or an air/gas fuel mixture, another is used for pumping the released methane, and the third one – to discharge any exhaust gases that may be emitted. Demirbas [17] estimates that the disintegration of clathrates requires only about 6% of the energy possible to be obtained from the released gas. However, this balance does not include the loss of energy that must be delivered to great depths. The assumptions of thermal stimulation technology for clathrates were introduced by Cranganu [18]. The method is based on the periodic delivery of fuel (preferably in the form of the extracted methane) with the air into the combustion chamber, ignition and discharging exhaust fumes after reaching the assumed pressure in the chamber. Methane is also discharged periodically, alternately with the fuel fed. The system can operate automatically through pressure and temperature sensors, which control the respective valves and the magneto. According to Cranganu [18], only 1.1–1.7% of the gas produced is consumed for the extraction of methane.

The method of depressurization is particularly suitable for obtaining methane from the clathrates lying in the vicinity of natural gas deposits. Natural gas extraction using conventional methods causes a decrease in pressure which destabilizes the adjacent clathrates, and the released methane feeds the gas deposit under operation [17]. In this way, methane was successfully obtained from clathrates in the Messoyakha area in northern Russia [19, 20]. Due to the necessity of a large pressure reduction, this method is not suitable for deep and highly super-cooled deposits [2]. To increase its efficiency, Bai et al. [21] suggest the use of additional thermal stimulation or an inhibition method at the end of the process.

The inhibition method introduces a chemical substance (inhibitor) to the clathrate-bearing layer to alter the conditions of the balance of the clathrates, i.e. to reduce the temperature of its stability. It is used commercially to prevent the formation of clathrates in natural gas pipelines. Substances acting as inhibitors may include, e.g. ethanol, ethylene glycol, diethylene glycol, and aqueous salt solutions: NaCl, CaCl₂, KCl, NaBr [20].

In a gas exchange method, carbon dioxide is introduced into the clathrate deposit in a gaseous form or as an aqueous solution. Methane occupies small and large cages in the clathrate structure, CO₂ occupies only large cages, forcing CH₄ out of them. It is estimated that in this way, without causing disintegration of a clathrate deposit, about 64% of the methane present in the deposit may be extracted. The reaction of CO₂ clathrate formation is exothermic – formation heat is 57.9 kJ/mol. The disintegration of methane clathrate is an endothermic process – its individual dissociation heat is 54.5 kJ/mol, and thus it is lower than the formation heat of CO₂ clathrate. As a result, the whole exchange process is exothermic [20]. Thus the method is based on heating and decay of methane clathrates by the heat released during formation of carbon dioxide clathrates after its injection into the deposit of methane clathrates. CO₂ clathrate stability zone is similar to the stability zone of CH₄ clathrates, except that CO₂ clathrates are more stable [22, 23]. Compared to CH₄ clathrates, CO₂ clathrates require lower pressure to achieve stability [24]. However, to secure a safe storage of CO₂, CO₂ injection must be stopped before reaching the CO₂ clathrate stability temperature. In the simulation of the process of CO₂ sequestration and simultaneous extraction of CH₄ using this method which was carried out by Maruyama et al. [25] only 6% of the resulting CO₂ was emitted into the atmosphere and the thermal efficiency of the whole process was 32%. A successful attempt to extract methane from clathrates by this method was undertaken in 2012 by the United States Department of Energy (DOE) in cooperation with ConocoPhillips and Japan Oil, Gas and Metals National Corporation [26]. A mixture of CO₂ and N₂ (probably simulating the content of typical exhaust fumes – the details were not disclosed) was pumped into the deposits on the north coast of Alaska, obtaining the release of methane in a continuous flow. The authors highlight that further field research is required to evaluate the effectiveness of CO₂ storage using this method. DOE is planning further pilot extraction tests in the Arctic

region and the commencement of a wider research program to examine the role of methane clathrates in the environment, taking into account their impact on global warming. Research is also conducted on the sequestration of CO₂, independent of the exploitation of methane clathrate deposits, by directly putting CO₂ into undersea sediments, where, under appropriate conditions of pressure and temperature, it will produce clathrates [27–29].

5. DISCUSSION

5.1. CLATHRATE OR HYDRATE?

Methane clathrate is usually referred to in the literature as a hydrate, which is inadequate from the point of view of chemical terminology. In chemistry, the term hydrate refers to compounds of a determined stoichiometric coefficient, which provide precisely defined quantities of water at dissociation. Most commonly, those compounds are salts containing water molecules in their crystals. However, these are not free water molecules, as it is the case of clathrates. In hydrates, water occurs in the form of separately attached hydrogen atoms and hydroxyl groups resulting from its dissociation. On the other hand, a clathrate compound is formed by a regular crystal structure of one compound (water) inside which – in “cages” formed by the hydrogen-bonded water molecules – the particles of another substance such as methane are unevenly arranged, whereas methane and water do not form chemical bonds. Clathrates are formed through crystallization from solutions or in the gas phase, when the “guest” molecules are trapped in the crystal lattice, if the dimensions of the “guest” match the dimensions of the cages within that lattice.

5.2. FEEDBACKS BETWEEN THE ENVIRONMENTAL EFFECTS OF METHANE CLATHRATE DESTABILIZATION

The main threat to our planet posed by the destabilization of massive methane clathrate deposits is global warming. Generally, two hypotheses explain the mutual connections between the release of methane from clathrates and climate change. One assumes that the disintegration of clathrates is the result of a pressure decrease caused by glaciation and the lowering of the sea level. Release of methane, in turn, leads to an increase in atmospheric temperature and the commencement of interglacial period. It may also cause an increase in temperature of the bottom layer and lead to degradation of further methane clathrate deposits. In this case, positive feedback occurs and the released gas causes further climate warming. On the other hand, the increase in temperature causes melting of ice caps and rising of sea levels, which increases pressure in the sediments, and – as a result of negative feedback – leads to the inhibition of

methane release from clathrates and to formation of new deposits. According to the second hypothesis, the increase in the temperature of oceanic water, which is a consequence of global warming, has a greater impact on the stability of clathrates than the increase in hydrostatic pressure resulting from rising sea levels [7]. As a result of global warming, the clathrates located at small depths decompose, and due to positive feedback it may lead to the release of methane from deeper deposits and acceleration of global warming, despite the rise in sea level. Clathrate destabilization – in addition to the enhancement of the greenhouse effect through the emission of unoxidized methane into the atmosphere – causes deoxygenation and decrease in pH of the oceans, which leads to the imbalance of ecosystems, including extinction of certain species of flora and fauna. Biological imbalance may also be enhanced by violent phenomena associated with the decomposition of clathrates, such as tsunamis. In this situation, methanogenic bacteria produce additional quantities of methane from dead organic matter in the formed anaerobic zones. Reduction processes taking place during anaerobic digestion of dead organic matter, especially proteins, lead also to the formation of toxic hydrogen sulphide, which enhances the aforementioned effect. The risks associated with the destabilization of methane clathrate deposits and their interrelations are shown in Fig. 3.

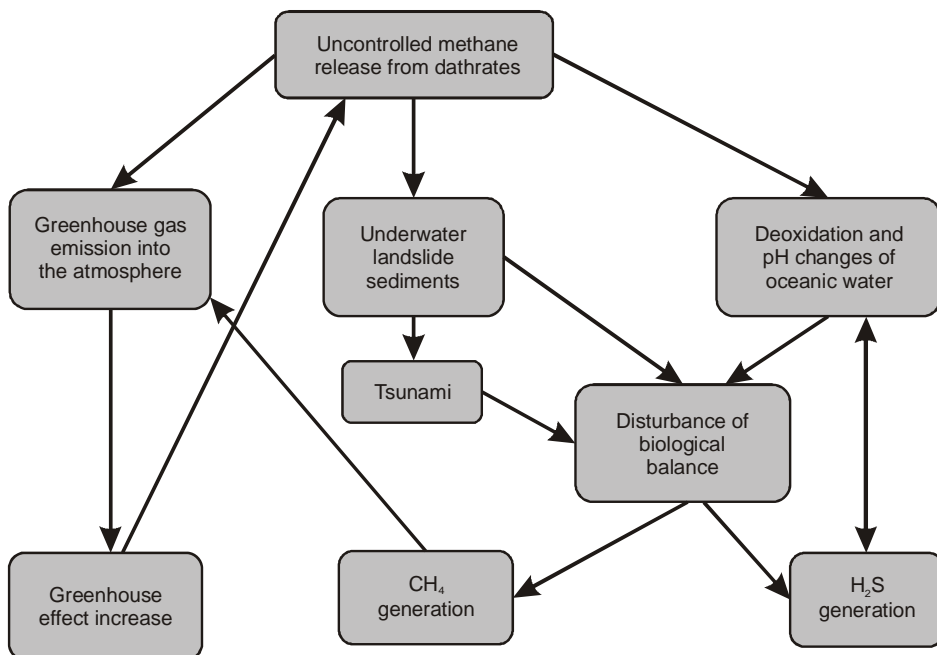


Fig. 3. Interrelations between the risks resulting from destabilization of methane clathrate deposits

5.3. THE ENVIRONMENTALLY SAFEST TECHNOLOGY FOR THE EXPLOITATION OF METHANE CLATHRATES SELECTION

With the search for technology of clean combustion of both conventional and unconventional fossil fuels, the most prospective method of exploitation of methane clathrates seems to be the method of CO_2 - CH_4 substitution. It may be particularly interesting for future power stations located near clathrate deposits – on the coast or on offshore platforms – which will be fuelled with methane extracted from these reserves. Carbon dioxide, absorbed from flue gases, e.g., by dissolving in the sea water, would be pumped into the clathrate deposit, resulting in the simultaneous release of methane (which could possibly be thermally assisted) and sequestration of CO_2 . It could therefore be an economically attractive version of the carbon capture and storage (CCS) method, which has recently been on decline, mainly because of the estimated operating costs now exceeding by an order of magnitude the price of CO_2 emission units. An important advantage of the method, in addition to the isolation of a greenhouse gas (CO_2) and a positive energy balance, is the increase in the stability of the deposit through the exchange of CH_4 to CO_2 . Worth developing, especially in the case of the exploitation of nearby conventional deposits of natural gas, is also the depressurization method. However, it is suitable only for the deposits at shallow depths. For such deposits, it may be considered to support this method by means of thermal and/or chemical stimulation. Due to the loss of energy when pressing the media to great depths and expensive chemicals, the use of the latter for clathrate deposits located at bigger depths seems too expensive and environmentally risky.

Despite numerous theoretical and experimental works on the methods of exploitation of methane clathrates, economic criteria for their selection have not been defined yet [2]. The estimates made under the United Nations Development Program [30] show that the extraction of methane from clathrates in convenient locations should not be more expensive than the acquisition of conventional natural gas. However, problematic may be potentially high transport costs due to the location of clathrate deposits far from the markets.

6. SUMMARY

The idea of the exploitation of methane clathrates raises hope to replace conventional energy sources, but it involves environmental hazards. Emission of CO_2 formed in the combustion of the obtained methane (excluding the situation when it replaces coal), and even more so methane emissions resulting from the destabilization of its deposits or release during transport, may contribute to the strengthening of the greenhouse effect.

Assuming average methane clathrate resources at 1500 Pg of carbon, it may be assumed that they would be sufficient to replace coal for over 200 years. Such an ex-

change would result in decreasing carbon dioxide emissions from fuel combustion by about 50%, while allowing sufficient time for establishing complete reliance of power industry on renewable energy. Further reduction of emission could be achieved by the use of CO₂ injection into methane clathrate deposits, thus supporting its production and creating more stable clathrates of CO₂. Gas exchange is the only method among the potential technologies of CH₄ clathrate exploitation which reduces the risks resulting from the destabilization of clathrate deposits. In this method, carbon dioxide formed during the combustion of methane can both be used for the extraction of this gas and be simultaneously sequestered. Despite being more stable than methane clathrate, CO₂ clathrate may also be destabilized due to the rise of global warming. However, the storage of CO₂ reduces its emissions and slows down the growth of its concentration in the atmosphere. As a result, global warming may be slowed down. Moreover, CO₂ clathrate resulting from the exchange stabilize CH₄ clathrate, thus reducing the risk of deoxygenation of ocean waters, sediment landslides and tsunamis. Therefore, controlled extraction of methane from clathrates using the technology of gas exchange, followed by its combustion, that is changing it into the gas with an over 20 times smaller greenhouse potential, may be a solution both to the problem of the depletion of conventional sources of fossil fuels, and to the problem of global warming. However, clathrate deposits are not renewable in a short time, so the extraction of methane from them will also be a temporary solution. The only permanent solution is to develop technologies of deriving energy from renewable sources.

The research should be intensified both on the impact of the current global warming on the stability of existing deposits of methane clathrates, and on the development of safe and cost-effective methods of controlled exploitation of methane clathrates.

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