Досліджено вплив механохімічно активованих домішок на процес утворення газових гідратів метану. Встановлено, що процес утворення газогідратів метану у присутності активованих алюмосилікатів відбувається не по автокаталітичному характеру. Виявлено, що у складі газового гідрату метану з'являється етан. Визначено константи швидкості утворення газогідратів метану при Т=274 К і тиску 5 МПа у присутності механоактивованих домішок

Ключові слова: газогідрати метану, механоактивація, гетерогенний каталіз, швидкість гідратоутворення, дисоціація, алюмосилікати, фазові перетворення

Исследовано влияние механохимически активированных добавок на процесс образования газовых гидратов метана. Установлено, что процесс образования газогидратов метана в присутствии активированных алюмосиликатов происходит не по автокаталитическому характеру. Обнаружено, что в составе газового гидрата метана появляется этан. Определены константы скорости образования газогидрата метана при Т=274 К и давлении 5 МПа в присутствии механоактивированных добавок

Ключевые слова: газогидраты метана, механоактивация, гетерогенный катализ, скорость гидратообразования, диссоциация, алюмосиликаты, фазовые превращения

EFFECT OF MECHANOACTIVATED CHEMICAL ADDITIVES ON THE PROCESS OF GAS HYDRATE FORMATION

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1. Introduction

Rising prices for traditional energy sources make it necessary to search for new approaches to solving energy problems. It is necessary, under modern conditions, to develop alternative energy projects [1]. The need to modernize a structure of coal and oil and gas complexes of the state [2–4] and to improve a mechanism for the development of the energy segment of Ukraine is also obvious [5, 6]. A possible solution is the introduction and application of the latest gas hydrate nanotechnologies, which can provide additional energy resources [7, 8].

We know that gas and water form crystalline compounds – gas hydrates (GH) under certain thermobaric conditions. They contain gas in the compressed concentrated state (up to 180 m^3 of gas/m^3 GH) [9, 10]. Gas hydrates are interesting from the fundamental and applied points of view because they are the objects of supramolecular (permolecular) chemistry. This is a relatively new field of science that investigates more subtle principle of organization of chemical matter. Its base is not specific chemical bonds only, but also favorable spatial complementarity of reacting components (RC). And a steric factor is the fundamental factor even in the presence of weak Van der Waals interactions between RC.

The main structural elements of GH are crystalline cells that have nanosize structures and consist of water molecules with gas molecules located inside [11].

Despite huge resources of natural gas, its role in the production of chemical products and secondary energy carriers is much lower: for example, a share of natural gas subjected to chemical processing is 5–7 % only. The main factor, which limits a widespread use of natural gas as raw material for chemical processing, is a relatively high stability of lower alkanes [12, 13].

However, a need to solve a set of problems associated with a low production rate and obtaining of a solid phase with a high content of gaseous hydrocarbons constrains a wide practical application of GH. The most common method for obtaining GH at laboratory and semi-industrial plants is based on the principle of movement of flows of a particular phase [14].

According to scientists, transportation of natural gas in the form of GH can be cheaper by 30 % than through trunk pipelines or transportation of hydrocarbon raw materials in a liquefied state [15].

In Japan, Germany and Norway, industrial plants of flow-through type equipped with a mechanical mixing device with a use of the principle of movement of flows of one or both phases produce synthetic GH [16]. In Japan, Mitsui Engineering & Shipbuilding Corporation built an experimental production of gas hydrate granules with a capacity of 5 tons/day based on a given technology [17].

Various technological solutions make it possible to intensify the process of hydrate formation by increasing a contact surface of phases. They accelerate the process of hydrate formation [18, 19]. Fine-dispersed water or solutions containing additives-promoters into the volume of gas, such as SAS (Surface Active Substance), high-speed mixing of

systems, including mixing by barbotage, etc. contribute to this [20–22]. Application of forced convection requires considerable energy consumption and complicates a design of installations for production of gas hydrates technically.

Thus, the study of GH formation under conditions close to natural is an urgent scientific task of great importance for solving global problems.

2. Literature review and problem statement

The issue of determination of prospects for the energy security of the state is especially important in an unstable situation in the Ukrainian gas market. This is possible by increasing volumes of own gas production, involving the use of methane of coal seams, gas fuel during processing of biological raw materials, obtaining bio and generator gases, and gas contained in gas hydrate deposits [23–25].

There is no methane production of gas hydrates on an industrial scale in the world. Japan plans to start it in 2018–2019. Nevertheless, a number of leading countries are implementing research programs. Scientists from the USA, Canada, Japan, Australia, Norway, India are working in this direction. The proposed technological solutions for extraction of methane gas from gas hydrate deposits described in [26–28] are of a theoretical nature. Industrial development of gas hydrates needs further experimental research. Therefore, issues related to justification of parameters of the effective process of dissociation of gas hydrate deposits are relevant and require a solution.

The study of properties of clathrate hydrates is necessary for improvement of modern technologies for gas production and gas transportation from gas hydrate deposits, creation of energy-saving technologies, development of hydrocarbon energy and technologies for separation of gas mixtures [29, 30]. A subsequent study of gas hydrate technologies and their application in practice is impossible without a detailed study of the kinetics of hydrate formation. This depends on a use of accelerators of the process directly. Accelerators are surface-active substances.

Japanese scientists and specialists of oil and gas companies obtained the most significant research results in studying the development potential of gas hydrate deposits [31].

A wide application of gas hydrate technologies is associated with an ongoing search for both optimal technologies for development of gas hydrate deposits [32–34] and production of gas hydrates for their use in transportation of hydrocarbon raw material [30, 35].

According to the Japan National Petroleum, Gas and Metals Corporation (JOGMEC) and the US Geological Survey, the "epoch of gas hydrates" will come no sooner than in 10–20 years. In particular, the International Energy Agency (IEA) does not take into account the "gas hydrate factor" in its long-term forecasts for the development of world energy. IEA experts believe that gas hydrates will not play a significant role until 2035, but they think it is necessary to monitor development of the direction closely.

Studies carried out on extraction and transportation of natural gas from gas hydrate deposits are theoretically possible, but they did not find practical application in the industry so far due to the lack of reliable and efficient technologies. The search goes in several directions, such as mechanoactivation (when uncovering reservoirs) and obtaining GH under conditions close to natural (using water solutions that simulate strata water [36]).

A work [37] shows that the mechanical activation (MA) of natural gas influences chemical transformations of hydrocarbons. Studies went in energy-intensive apparatuses such as ball mills.

Studies showed that MA of hydrocarbons leads to the processes of their destruction to lower molecular homologs and hydrogen. Initiation of chemical reactions involving hydrocarbons occurs due to formation of active radicals on surfaces of solids, which take part in mechanical loading [38]. A local temperature arises at point of "grinding body-substance" contact at the moment of impact in high-voltage apparatus. The phenomenon initiates chemical transformations of hydrocarbons during mechanical activation [39].

Authors of paper [40] carried out experimental studies on increasing of a contact area of a liquid and a gas phases to accelerate the reaction of obtaining gas hydrates, as well as to increase their gas content. They accelerated the process of hydrate formation by using a metal chamber with an additional area of S_{ch}=215 cm^2 and a polymeric structure of polytetrafluoroethylene, which were installed inside chambers-reactors. They found out that a larger increase in time of a synthesis of hydrates of natural gas leads to an increase in a volume of gas in the solid phase. Thus, there is an increase of a gas content in a hydrate in 2.6 times at an increase in duration of the synthesis of hydrates of natural gas in 4 times. There is an increase in a content of hydrocarbons in the hydrate phase. Natural gas in the hydrated state under intensive mechanical action undergoes chemical transformations, which promote processes of elongation of a carbon skeleton of gaseous hydrocarbons. They found out that mechanochemical transformations of hydrocarbons – components of natural gas directed towards elongation of a chain, proceed only when natural gas transforms to the hydrate state.

The second direction is the production of gas hydrates in the presence of artificial strata water. As we know, about 98 % of gas hydrate deposits are aquamarine and concentrated on the shelf and continental slope of the World Ocean [41]. This is due to the fact that the bottom of the world ocean has the most favorable combination of temperature and pressure for hydrate formation and creates conditions for the formation of hydrate formation zones on 90 % of its area [42, 43]. Aquamarine hydrates are in equilibrium with sea water, the main component of which is sodium chloride. In papers [44, 45], objects of the study are hydrates of natural gas synthesized in solutions of sodium and calcium chlorides. Concentrations of sodium chloride solutions are 5, 10 and 15 %, which corresponds to a total mineralization of brines of 51.8; 107.1, and 166.3 g/l.

A chemical nature of salts affects processes of formation and decomposition, as well as a texture of hydrates of natural gas [46, 47]. Formation of hydrates in solutions of sodium chloride proceeds more slowly than in solutions of calcium chloride. Studies established that granular GH appear in sodium chloride solutions, and layered GH – in solutions of calcium chloride. A larger volume of natural gas with a larger average molecular mass concentrates in granular hydrates. A study of the kinetics of decomposition of GH obtained from different liquid phases showed that granular hydrates decompose more slowly than layered hydrates. A rate of decomposition of both types of gas hydrates increases at an increase in mineralization of solutions.

Ways and methods of GH obtaining differ from each other in their complexity only. Authors of work [48] applied static conditions without external mechanical influences on a system to obtain artificial gas hydrates. The driving force of the process was a temperature factor. They determined a cooling regime, which made possible to extract gas hydrates of methane, ethane and natural gas with high gas saturation from water, as a result of investigations in high pressure chambers-reactors of the closed-type. They found that the maximum value of the specific gas content is characteristic of GH, which is a snow-like dense structure, obtained of ice workpieces with dimensions not exceeding 4 cm in diameter in the temperature range from 268 to 278 K.

The process of formation of gas hydrates in nature is of a deep type, i.e. retention and passage of gas particles occurs in a volume of the bottom soil. At the same time, filtration-capacitive properties of rocks, which contain gas, change significantly [49]. The formation of GH under conditions is possible by two mechanisms:

1. GH form on contacts of grains, which are the weakest elements of a structure.

2. GH cement the matrix of a sediment, they form in pores outside contacts between grains, and therefore they have little or no effect on the cohesion of rock particles, which leads to a decrease in the porosity of a sediment.

Results show that a crystalline hydrate is a separate phase included in a pore, which reduces the porosity of a rock. However, the results are for synthetic surfaces with properties close to quartz only [50].

Thus, the results of fundamental studies of the mechanism of GH formation, as well as data on the effect of mechanically activated additives on the hydrate formation process, can significantly affect the technology of obtaining of gas hydrates. Researchers did not study the hydrate formation mechanism sufficiently due to difficulties of the experimental nature. However, studies on the mechanism of GH formation under conditions close to natural conditions are prerequisite for improvement of the technology of obtaining of artificial methane hydrates.

3. The aim and objectives of the study

The aim of present study is to produce GH of methane with a high gas-hydrate-formation content in the solid phase in an isolated system at a change in pressure and presence of mechanically activated rocks close to the bottom rocks in a chamber.

We set and solved the following tasks to achieve the objective:

– to determine effect of mechanically activated additives on the gas hydrate formation process;

– to define the composition of gas in GH during the process in the presence of activated additives;

– to determine the rate constant of GH formation in the presence of activated additives.

4. Materials and methods to study the mechanism of gas hydrate formation of methane in the presence of mechanically activated additives

4. 1. Essence of the study

We carried out synthesis of GH of methane in an installation for gas hydrates production. The installation makes it possible to model thermobaric conditions similar to natural ones. The NPO-5 installation designed at the National Mining University (NMU) (Dnipro, Ukraine) makes it possible to study high-speed production of GH of methane under "soft" conditions, varying a temperature (from +0.5 to +10 °C) and pressure (from 1 to 10 MPa) [51, 52]. Next, in accordance with the previously developed technique [53], we filled the chamber with a mechanically activated mineral, and the process of production of GH of methane began.

We used aluminosilicates of a natural composition as mechanically activated additives. We carried out mechanochemical activation of materials in a vertical vibrating mill (VVM). Its main advantage is a shortening of a time for grinding of powders – on the one hand, and on the other hand, not only a surface activation of material occurs, but also a violation of the internal structure of particles at vibro-impact activation. Thus, we can observe penetration of an active zone into a greater depth [54], which leads to volumetric ionization of the activated material.

We applied a method for estimation of a granulometric composition of powders by a specific surface, which is a convenient dispersion characteristic, to establish a dispersion constant [55]. We determined a specific surface by the rarefied gas filter resistance. A base of the method is the theory of rarefied gas flow through a system of solid spheres, developed by B. N. Deryagin, when a length of a path of gas molecules is much greater than a distance between balls (Knudsen flow mode) [56]. The error of the method is 1 %.

We determined an average size of ground particles using data obtained with SK LAZER MICRON SIZER PRO-700 laser analyzer (Japan). Formation of the activated state is closely connected with energy characteristics of material [57]. According to the above, we used a universal method for studying energy characteristics of materials by potentiometric measurements in suspensions with an indifferent electrode. The method of potentiometric measurements [58] makes it possible to calculate a potential curve and a total adsorption potential.

We obtained diffractograms *in situ* using the DRON-2 X-ray diffractometer ("Burevestnik", Russia). We determined phase analysis of materials applying the DRON-3 X-ray diffractometer ("Burevestnik", Russia): radiation Fe $K\alpha$, high voltage 35 eV, anode current 20 mA. We studied physical and chemical processes, which occur in the production of GH of methane, employing differential thermal analysis (DTA) and X-ray fluorescence analysis (XFA) methods. We investigated a composition of gaseous products by gas-adsorption chromatography using the "LXM-2000-TM" chromatograph ("Electra", Russia).

4. 2. The procedure for obtaining mechanically activated additives, as well as the study of the rate of hydrate formation in their presence

We carried out mechanoactivation of minerals in the installation, which is a VVM laboratory [59, 60], designed and manufactured at NMU. Experiments on mechanoactivation of minerals went in continuous and periodic modes. We used grinding chambers of different design for experiments. In continuous mode, material from a bunker-feeder enters a grinding chamber, passes through it L path, m and then goes to a bunker-receiver. The height of a grinding chamber and a number of passes of the material through it determine L value. In periodic mode, we pour a weighed portion of material into a chamber, close it hermetically and grind material for

a specified time. In this case, we fix the mass of a portion of grinded material.

In the periodic mode, material gets into a chamber in advance. A cover of a chamber closes hermetically to prevent contamination of the environment. When an electric motor is turned on, a grinding chamber performs rectilinear vibrational movements in a vertical plane with a specified amplitude (7 mm) and a frequency (16 Hz). Grinding bodies interact with each other, as well as with the bottom and a cover of a grinding chamber at the moments of passage of the top and bottom dead points.

An important factor, which affects the efficiency of the grinding process in VVM mill is a gap between the top layer of balls and a cover of a grinding chamber, which depends on the degree of filling a chamber with balls. As a result of preliminary tests, we found that for balls of diameters of 6 and 9 mm, the maximum energy intensity of the technological loading takes place at a value $\Delta=9-20$ mm and depends little on a total height of a layer of balls in a chamber.

We conducted laboratory studies in two stages. At the first stage, we determined the most rational technological parameters of grinding, which made it possible to obtain the best result in terms of the specific surface area. The diameter of grinding bodies and the ratio of masses of material to be grinded and the technological load varied in the course of the experiment.

The grinding bodies were spheres of diameter d_b of 6 and 9 mm. A gap between balls and the chamber cover in all experiments was 10 mm. The mass of portions of the grinded material m_m was 1/20 and 1/40 of the mass of balls m_b. We took powder samples at certain intervals. We observed them with a microscope to study a shape of particles and to estimate a granulometric composition of the material obtained. We opened the chambers after cooling of a room temperature only in each case. We returned powder samples to the chambers for further grinding after the examination with a microscope. Thus, we established a diameter of balls d_b, at which the most effective grinding of the materials took place. We could not asses an influence of the parameter m_m/m_b on a granulometric composition of the grinded product visually. We carried out experiments with a use of technical methods of laboratory analysis to refine the data obtained.

We used the accepted diameter of grinding bodies in the following experiment. Only the ratio of masses of the grinded material and the technological load changed in it. Here, in addition to visual observation, we measured a specific surface area also. We determined the best ratio of the powder mass to the mass of balls m_m/m_b by the maximum value of the specific surface area S_{sp}.

We used the determined optimal grinding mode in the second stage of the study. We performed a physical and chemical analysis for mechanically activated samples: DTA and XFA [61].

We determined a rate of hydrate formation of methane by the kinetic method at the initial rate of formation of an ice crust, and then we calculated an amount of methane per unit volume (C_m) for different mechanoactivation of additives.

We determined measurement of the volume of methane in GH, as well as the composition of gases formed, in two ways:

– the first one, by measurement of a volume of gas entering the reactor at high pressure; but this method is very difficult, since there are no measurement devices, which measure a small amount of a passing gas at high pressure;

– the second one, by measurement of a volume of gas, which leaves the reactor during decomposition of the hydrate; in this case, pressure is small, which makes possible to use household gas meters operating at a pressure less than 1 MPa.

Fig. 1 represents the experimental installation (NMU, Dnipro, Ukraine) intended for obtaining of artificial gas hydrates of various composition under various conditions of their formation. This makes it possible not only to synthesize, but also to investigate GH samples.
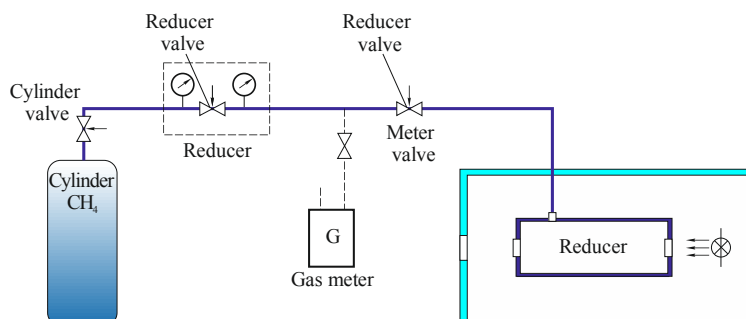

Fig. 1. Schematic of experimental installation

We determined C_m according to the following procedure:

1. We decreased the temperature in climate chambers, and, respectively, in the hydrate formation reactor, from +1 to −10...15 °C after the completion of the process of GH obtaining (when all water reacted). We observed the process of hydrate formation in the reactor through a window in the chamber and the reactor.

2. We closed the valve of the gas cylinder and the valve of the reducer.

3. We disconnected the high-pressure hose from the reducer and connected it to a gas meter.

4. We opened the reactor valve and the temperature raised to a room temperature in the chamber and in the reactor.

5. Methane hydrate began to decompose. The extracted methane passed through the gas meter and we determined its quantity.

We calculated C_m knowing the value of the extracted gas and the volume of water poured into the reactor. Then, we reduced gas pressure in the reactor by 1 MPa and repeated the process. We determined the composition of the obtained gas chromatographically.

5. Results of studies of the effect of mechanically activated additives of aluminosilicates on the rate of gas hydrate formation

We obtained heterogeneous activated additives, which are analogues of natural formation media of gas hydrates in nature to accelerate the formation of the gas hydrate. Natural gas hydrates are metastable minerals, formation and decomposition of which depend on pressure and temperature, composition of gas and water and properties of a porous medium where they are formed [62, 63]. Fig. 2 shows main types of formation of natural GH.
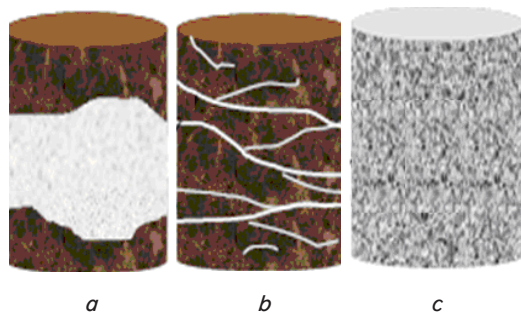
Fig. 2. Types of formation of natural gas hydrates: *a* — a massive layer of hydrate; *b* — filling of large and small cracks; *c* — filling a porous space of the permeable rock

Fig. 3. Microstructures of activated additives (2000^x) formed during vibro-impact loading over the period: *a* — 5 minutes; *b* — 20 minutes; *c* — 40 minutes

The following important conditions are necessary for the formation of accumulations of hydrates: heterogeneity of a geological space, temperature field, permeability field, salinity of water [63]. It is also necessary to consider the following factors:

– mineralogical, granulometric and microaggregate compositions of soils;

– their humidity and density;

– mineralization of a pore solution;

– presence of clay particles and organic impurities.

The first task of the study was to obtain analogues of natural media by mechanoactivation. Studies showed that sediments, which consist of products of land destruction, such as pebbles, boulders, gravel, silt, and sand, cover almost all the shelf space. In some places the shelf is covered with remains of marine animals, mostly seashells. And there are outcrops of naked solid rocks – granite, basalt in places where strong sea currents prevail. We chose tectosilicates for experimental studies.

We carried out mechanoactivation in 4 modes. We changed the diameter of balls (d_b=6 and 9 mm), the ratio of the mass of milling bodies and the activated material (n=1/20 and 1/40). From the experimental data we found out that parameters of grinding of the rational mode of vibroactivation are: d_b=9 mm and n=1/40.

Fig. 3 shows microstructures of tectosilicates formed during vibro-impact activation.

From the point of view of the change in a crystalline structure of tectosilicates during vibro-impact activation, the process of transition from the crystalline state to the amorphous state occurs. Moreover, formation of an amorphous structure occurs not only on the surface of a substance, but also in the volume of a layer of the activated product. We performed X-ray analysis and microscopy of samples to control the structural state during the mechanoactivation process. Table 1 presents X-ray diffraction data.
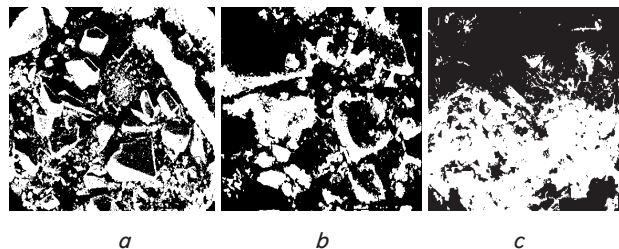
Table 1 shows that mechanoactivation is connected with formation of a defect structure on the surface of the basic structure (aluminum oxide). Basically, microcrystals and crystallites of aluminosilicates appear. A nature of changes in the substructure of microdistortions in the crystal lattice ($\Delta d/d$) and an increase in concentrations of surface dislocations ($1/D^2$) proves this.

Particles consist of relatively small crystallites with anisotropic effective dimensions of the mosaic blocks after a 5-minute vibro-impact loading, according to the data. Anisotropy of blocks is due to the presence of packing defects (PD) in α-Al$_2$O$_3$ with hexagonal close packing (HCP). A crystalline structure is characteristic for particles after a 10-minute vibro-impact loading. Crystallites appear in α-Al$_2$O$_3$, apparently because of the development of the process of destruction in the region of large-angle grain boundaries. For the powder obtained after a 20-minute loading, the dispersion of structure fragments is higher, and particles almost do not contain PD. This is due to the fact that the effective size of mosaic blocks in different crystallographic directions is almost the same. The powder obtained 90 minutes after mechanochemical activation consists of molecular-dense aggregates.

We chose three samples corresponding to 5, 20, and 40 minutes of activation to carry out GH formation reaction. A base of the choice is a cost of thermal energy (Q) needed to produce 1,000 m^3 of methane gas. Work [64] proves that the value of Q increases in parabolic dependence with an increase in the proportion of rock inclusions (η) in gas hydrate deposits. There is a new classification of gas hydrate deposits based on the content of rock inclusions in the deposits taking into account peculiarities of gas saturation in the bottom sediments of the Black Sea. The classification is based on energy costs when developing gas hydrate fields to produce 1000 m^3 of methane gas. Thus, we propose to divide deposits of gas hydrates into 4 classes dependet on the number of rock inclusions in the gas hydrate massif (Fig. 4).

Table 1

Characteristics of activated samples

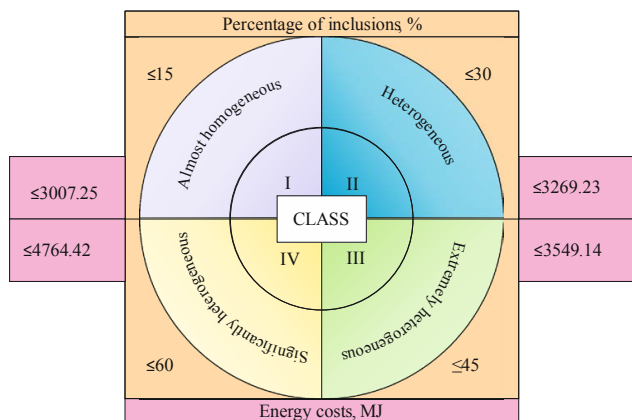| Time of material processing, min | Substructure parameters | | | Crystallinity degree, % | Average size structural fragments | | | |
	Size of crystal lattice, *D*, nm	Concentration of surface dislocations, $1/D^2$, 10^{-14} m^{-2}	Defectiveness, $\Delta d/d$, 10^3		Particle, μm	Crystallite, μm	Mosaic block in the direction of planes, nm	
							012–024	113–226
initial	92.0	1.18	1.2	100.0	–	–	–	–
5	93.0	1.15	1.25	100.0	–	3.2	100.0	45.0
10	94.0	1.07	1.4	97.0	–	3.3	100.0	52.0
20	80.0	1.56	1.9	95.0	2.4	3.0	63.0	61.0
40	71.0	2.03	2.2	70.9	–	2.6	53.0	60.0
90	59.0	2.87	2.7	20.0	–	2.0	50.0	50.0

Fig. 4. Classification of gas hydrate deposits by energy costs

Another justification for the use of activated media in the activation process is their increased catalytic activity due to the formation of active centers on a surface [65].

Fig. 5 shows the kinetic curve of the formation of GH of methane without addition of aluminosilicate (activation – 5 minutes).
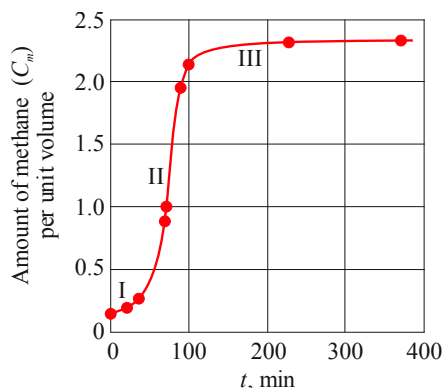

Fig. 5. Typical kinetic curve of the formation of GH in presence of mechanically activated additives (5 minutes)

The curve in Fig. 5 has an autocatalytic character, which is related to a different structure and, correspondingly, to gas saturation of the methane gas hydrate formed by addition of a mechanochemically activated additive. The kinetic curve has a complex form, which indicates the ambiguity of a mechanism of GH formation:

– *Stage I* – a period of induction, i. e., accumulation of methane in the activated rock, where a process of water structuring and beginning of a process of saturation of the structure with methane prevails;

– *Stage II* – progressive GH methane formation and, correspondingly, maximum gas saturation rate; there is a need to spend additional energy on formation of clathrates;

– *Stage III* – beginning of a process of saturation of clathrates and establishment of equilibrium, in which the structure of a clathrate does not change.

The process of GH formation on mechanically activated surfaces leads to a change in kinetic curves. Induction period decreases in dependence on the degree of activation, and disappears on the sample corresponding to 20-minute activation.

Fig. 6 shows semilogarithmic anamorphosis. However, it has three knees that correspond to a change in the hydrate formation mechanism at T=274 K and pressure of 5 MPa

in the presence of mechanically activated additives. We determined the rate constants for methane GH formation graphically.

We calculated the rate constants of hydrate formation based on semilogarithmic anamorphosis. Table 2 gives the calculated data.
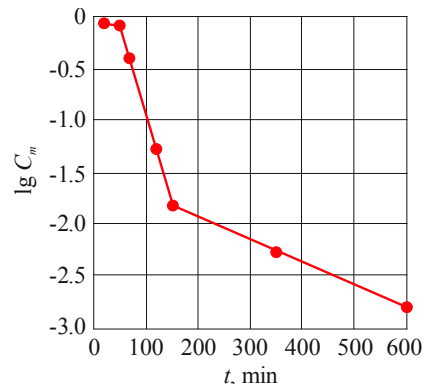

Fig. 6. Semilogarithmic anamorphosis of the process of methane GH formation in the presence of activated additives

Table 2

Constants of hydrate formation at T=274 K and pressure of 5 MPa in the presence of mechanically activated additives

Material	Rate constants of GH formation, hour^{-1}		
	1-st stage, k_1	2-nd stage, k_2	3-rd stage, k_3
Activated aluminosilicates 20 minutes	1.20×10^{-2}	8.20×10^{-2}	1.25×10^{-2}

Thus, during formation of gas hydrates, a rate of chemical reaction, as well as a rate of coal gasification, is self-catalyzed due to natural minerals [66].

We made electron microscopic images of particles formed during the process, and measured energy characteristics of the activated surface by potentiometric titration method. The method of potentiometric measurements makes possible to calculate a potential curve and a total adsorption potential.
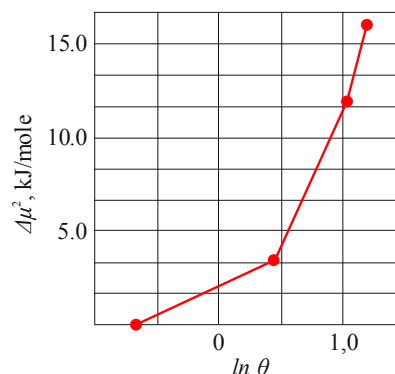

Fig. 7. Potentiometric curve of mechanically activated aluminosilicate

Fig. 7 shows a general view of the potential curve of a mechanically activated aluminosilicate additive.

We built the potential curve in the coordinates $\Delta\mu^2$–$\ln\theta$, where $\Delta\mu$ is a conditional adsorption potential calculated on the experimental data; θ is a degree of filling of a surface for iron ions calculated on the experimental data also.

The curve consists of several rectilinear sections, each of which corresponds to adsorption on a certain type of adsorption-active centers. The curve makes possible to calculate the following parameters:

– a real area per one sorbed ion Fe(III), nm^2;

– θ_{01} is a value of θ at the point of intersection of the first section of the potential curve with the abscissa axis (Fig. 7), and θ_{0i} is a degree of filling of a surface by this type of adsorption-active centers corresponding to the point of intersection of the section with the abscissa axis;

– $\Delta\mu_{ai}$ is a value of the adsorption potential at the maximum of distribution of a given kind of centers, kJ/mol;

– $\Delta\mu_{\Sigma i}$ is a total adsorption potential of each kind of centers, kJ/mol;

– $\Delta\mu_{\Sigma}$ is a total surface adsorption potential, kJ/mol.

Table 3 gives the results of calculation of parameters.

Table 3

Data on the calculation of parameters of active surface centers

Grinding time	$\delta\theta_i$	$\Delta\mu_{ai}$, kJ/mol	$\Delta\mu_{\Sigma i}$, kJ/mol	$\Delta\mu_{\Sigma}$, kJ/mol	Type of adsorption active centers
α-Al$_2$O$_3$, initial	0.05	0.02	0.07	0.13	Active oxygen Coordinated-bound water
	0.02	0.60	0.06		
5 minutes	0.26	0.60	0.37	0.96	Active oxygen Coordination-bound water OH-group
	0.13	1.30	0.30		
	0.09	2.09	0.29		
20 minutes	0.52	1.20	0.79	1.97	Active oxygen Coordination-bound water OH-group
	0.26	2.50	0.60		
	0.18	4.18	0.58		
40 minutes	0.40	1.02	0.57	1.41	Active oxygen Coordination-bound water OH-group
	0.19	1.90	0,46		
	0.14	2.08	0.38		

From the data of Table 3, we see that 3 types of adsorption-active centers appear on the surface of mechanically activated samples:

– OH$^-$ group ($\Delta\mu_a$=4.18);

– coordinated-bound water ($\Delta\mu_a$=2.5);

– active oxygen ($\Delta\mu_a$=1.2).

Potentiometric studies show that a sample activated for 20 minutes is more active. Water associates are reforms with the subsequent formation of water frameworks of pentagonal dodecahedrons as a result of the reaction of methane GH formation on activated surfaces. Such structures appear in liquid water before formation of hydrate-forming molecules.

Moreover, we found peaks corresponding to formation of a methane-ethane homologue during the chromatographic analysis of gaseous substances. Thus, a cryochemical synthesis of hydrocarbons occurs, catalysts of which are activated additives, in the formation of methane gas hydrates in presence of mechanically activated additives. Naturally, further mechanochemical transformations take place when GH itself is activated.

Table 4 gives results of chromatographic studies of methane GH obtained with the addition of aluminosilicates of varying degrees of activation.

We did not obtain such results by chance. A region with a local temperature of about 650 °C appears at vibro-impact activation (at the moment of impact), which leads to dehydroxylation of a surface and is accompanied by formation of coordinatively unsaturated cations. Infrared spectroscopy and nuclear magnetic resonance (NMR) methods confirm this effect. There is a diagram of formation of coordination-unsaturated cations on a surface of aluminosilicates below (Fig. 8).

Table 4

Results of mechanochemical synthesis of ethane in the production of methane GH

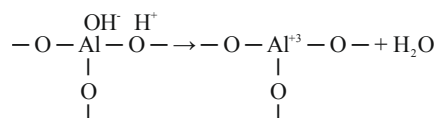| Inclusion class	Activation time of aluminosilicates, min	Maximum amount of methane in methane GH, %	Amount of ethane formed in methane GH, %
I	40	96	4
II	20	94	6
III	5	95	5

$$-O-Al-O- \rightarrow -O-Al^{+3}-O-+H_2O$$

Fig. 8. Diagram of coordination-unsaturated cations

Formation of such coordinatively unsaturated cations (Fig. 8) leads to an increase in the activity of compounds, since the coordination-unsaturated ions with half-filled electron shells can be regarded as free valences on a surface.

Thus, the formation of methane GH in the presence of mechanochemically activated additives leads to the synthesis of higher homologues of hydrocarbons.

6. Discussion of results of study of the effect of mechanically activated additives on the process of hydrate formation of methane

Thus, we found out that GH formation in presence of mechanically activated aluminosilicates has an autocatalytic mechanism, during operation of which a process of nucleation of a new phase occurs on activated aluminosilicates.

The complexity of the process lies in the fact that behavior of water molecules immediately surrounding a gas molecule differs from water molecules in the volume. There are many impurities in sea water: dissolved substances, colloids, suspensions, living organisms and products of their vital activity. The impurities in the ocean, as in a large-scale reservoir, settle gradually to the bottom and form bottom sediments. The uppermost layer of the sediments forms the bottom soil, a surface layer of the lithosphere beneath the ocean.

In accordance with the nature of the source material out of which bottom sediments form, they are divided into two main types: terrigenous and organogenic, or biogenic. Such division is conditional to a large extent, as sediments of both types are not strictly localized in nature, and the assignment of soil to one or another type is determined by a degree of predominance of organogenic or terrigenous sediments.

Thus, silty compounds are practically aluminosilicates of different composition with admixtures of metal oxides - iron, magnesium, titanium, calcium, etc. Although clay minerals have low adsorption and catalytic activity in the natural

state, they can be activated due to ion exchange, therefore, this makes possible to regulate their porous structure. The activation leads to a sharp increase in a surface and a volume of mesopores, which is associated with formation of amorphous silica, which has pores available not only for water molecules, but also for hydrocarbons.

A passage of gases through the medium includes the following cases:

– penetration through pores;

– penetration through cracks;

– complete obstruction of a canal mouth.

Fig. 9 shows the course of gas through mechanically activated samples (analogous to natural soils) schematically.

Obstruction of a mouth of one of canals (Fig. 9, *a*, 1) leads to the cessation of movement of a liquid in it for an ideal system. A labyrinth system of interconnected canals provides for opening of a side canal (Fig. 9, *b*, 1') with a mouth of smaller or larger diameter if a main canal is obstructed. Due to the opening of side canals, a partial compensation of the drop in permeability occurs at obstruction of mouths of main canals. It is obvious that the inclusion of channels with mouths of smaller diameter in operation occurs when pressure in the system increases.
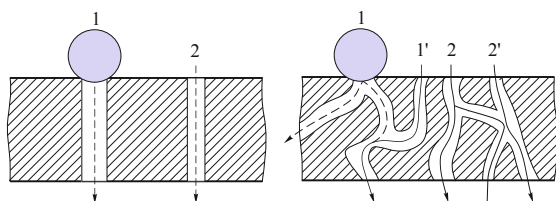

Fig. 9. Diagram of gas movement and capillary obstruction in ideal (1) and real (2) systems

The mechanism of passage of gas particles through the soil with the formation of gas hydrates is a physical and chemical mechanism of retention, which is called sorption mechanism sometimes. It includes various intermolecular interactions with different binding energies, as well as physical bonds, van der Waals bonds, dispersive bonds, and others.

We can observe the phenomenon of obliteration during operation of the physical and chemical mechanism of particle retention, that is, fouling of walls of capillaries of the soil, which leads to a decrease in the live section of capillaries. The increase in pressure promotes an increase in the rate of a liquid or gas in capillaries, which can cause particles to break off from walls of capillaries under certain conditions and carry them to the gas hydrate. We studied the effect of microcatalysts on the hydrate formation process during the research.

The mechanism of passage of gas particles through the soil with the formation of gas hydrates is a physical and chemical mechanism of retention, which is called sorption mechanism (SM) sometimes. SM includes various intermolecular interactions with different binding energies, as well as physical bonds, van der Waals bonds, dispersion bonds and others.

We did not consider a diffusion component of the gas hydrate production process in the study, although there were such attempts earlier [67]. The studies show possibility of carrying out heterogeneous catalysis at low temperatures and are a continuation of the development of cryochemical synthesis methods.

7. Conclusions

1. We established that the formation of methane gas hydrates in presence of mechanically activated aluminosilicates is not autocatalytic, but an increase in the reaction rate is connected with formation of three types of adsorption-active centers on a surface of mechanically activated samples with the following potentials: OH^- group ($\Delta\mu_a$=4.18); coordination-bound water ($\Delta\mu_a$=2.5); active oxygen ($\Delta\mu_a$=1.2).

2. We found out that up to 6 % of ethane appears during the chromatographic analysis of gaseous substances in the gas hydrate of methane, in dependence on the degree of activation.

3. We determined that the semilogarithmic anamorphosis has three knees, and this shows a change in rate constants of the formation of GH of methane and, accordingly, a change in the hydrate formation mechanism at T=274 K and pressure of 5 MPa in presence of mechanically activated additives. We calculated three rate constants for the formation of GH methane, which vary from 1.20×10^{-2} to 1.25×10^{-2} hour^{-1}, based on semi-logarithmic anamorphosis.

This study addresses the production of gas hydrate of methane with a high gas-hydrate-forming content in a solid phase in the isolated system at T=274 K and pressure of 5 MPa and presence of mechanically activated rocks close to the bottom of the chamber.

We used mechanically activated samples of various degrees of grinding to increase an area of contact surface of heterogeneous phases. We carried out mechanochemical activation of materials in a vertical vibrating mill (VVM).

In the study, we found out that formation of gas hydrates on activated aluminosilicates leads to the cryochemical synthesis of hydrocarbons, due to formation of additional reaction centers formed upon activation. This indicates a change in the mechanism of formation of GH during the process. We calculated three rate constants for the formation of GH of methane, which vary from $1.20 \cdot 10^{-2}$ to $1.25 \cdot 10^{-2}$ hour^{-1}, based on semi-logarithmic anamorphosis. The study showed that formation of methane gas hydrates in presence of activated additives leads to formation of up to 5–6 % of ethane. Chromatographic method confirmed this.

This indicates possibility of carrying out a low-temperature synthesis of higher hydrocarbons in the artificial production of GH, in contrast to the known mechanochemical transformations during the process of obtaining gas from gas hydrates.

Keywords: methane gas hydrates, mechanoactivation, heterogeneous catalysis, rate of hydrate formation, dissociation, aluminosilicates, phase transformations.

References

1. Basu, R. (2017). Evaluation of some renewable energy technologies. Mining of Mineral Deposits, 11 (4), 29–37. doi: 10.15407/mining 11.04.029
2. Tabachenko, M., Saik, P., Lozynskyi, V., Falshtynskyi, V., Dychkovskyi, R. (2016). Features of setting up a complex, combined and zero-waste gasifier plant. Mining of Mineral Deposits, 10 (3), 37–45. doi: 10.15407/mining10.03.037
3. Lozynskyi, V. G., Dychkovskyi, R. O., Falshtynskyi, V. S., Saik, P. B., Malanchuk, Ye. Z. (2016). Experimental study of the influence of crossing the disjunctive geological faults on thermal regime of underground gasifier. Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, 5, 21–29.
4. Khomenko, O., Kononenko, M., Myronova, I. (2013). Blasting works technology to decrease an emission of harmful matters into the mine atmosphere. Mining of Mineral Deposits, 231–235. doi: 10.1201/ b16354-43
5. Fomychov, V. (2016). Efficiency of energy resource production while optimizing parameters of socio-economic balance. Mining of Mineral Deposits, 10 (1), 89–95. doi: 10.15407/mining10.01.089
6. Kononenko, M., Khomenko, O. (2010). Technology of support of workings near to extraction chambers. New Techniques and Technologies in Mining, 193–197. doi: 10.1201/b11329-32
7. Max, M. D., Johnson, A. H. (2016). Deepwater Natural Gas Hydrate Innovation Opportunities. Exploration and Production of Oceanic Natural Gas Hydrate, 173–194. doi: 10.1007/978-3-319-43385-1_6
8. Carroll, J. (2014). Natural gas hydrates: A guide for engineers. Oxford, United Kingdom: Elsevier, 340.
9. Gas hydrate (2007). Hawley's condensed chemical dictionary. John Wiley & Sons, Inc. doi: 10.1002/9780470114735.hawley07697
10. Boswell, R. (2009). Is Gas Hydrate Energy Within Reach? Science, 325 (5943), 957–958. doi: 10.1126/science.1175074
11. Max, M. D., Johnson, A. H. (2016). Commercial Potential of Natural Gas Hydrate. Exploration and Production of Oceanic Natural Gas Hydrate, 355–394. doi: 10.1007/978-3-319-43385-1_11
12. Dychkovskyi, R., Lozynskyi, V., Saik, P. (2018). Modeling of the disjunctive geological fault influence on the exploitation wells stability during underground coal gasification. Archives of Civil and Mechanical Engineering. doi: 10.1016/j.acme.2018.01.012
13. Pivnyak, G., Bondarenko, V., Kovalevs'ka, I., Illiashov, M. (2013). Mining of mineral deposits. CRC Press, 382. doi: 10.1201/b16354
14. Mohebbi, V., Behbahani, R. M. (2014). Experimental study on gas hydrate formation from natural gas mixture. Journal of Natural Gas Science and Engineering, 18, 47–52. doi: 10.1016/j.jngse.2014.01.016
15. Siažik, J., Malcho, M. (2017). Accumulation of Primary Energy Into Natural Gas Hydrates. Procedia Engineering, 192, 782–787. doi: 10.1016/j.proeng.2017.06.135
16. Takahashi, M., Moriya, H., Katoh, Y., Iwasaki, T. (2008). Development of natural gas hydrate (NGH) pellet production system by bench scale unit for transportation and storage of NGH pellet. Proceeding of the 6 International Conference on Gas Hydrates.
17. Watanabe, S., Takahashi, S., Mizubayashi, H., Murata, S., Murakami, H. (2008). Demonstration project of NGH land transportation system. Proceeding of the 6 International Conference on Gas Hydrates.
18. Abbasian Rad, S., Rostami Khodaverdiloo, K., Karamoddin, M., Varaminian, F., Peyvandi, K. (2015). Kinetic study of amino acids inhibition potential of Glycine and l -leucine on the ethane hydrate formation. Journal of Natural Gas Science and Engineering, 26, 819–826. doi: 10.1016/j.jngse.2015.06.053
19. Sa, J.-H., Kwak, G.-H., Han, K., Ahn, D., Cho, S. J., Lee, J. D., Lee, K.-H. (2016). Inhibition of methane and natural gas hydrate formation by altering the structure of water with amino acids. Scientific Reports, 6 (1). doi: 10.1038/srep31582
20. Semenov, M. E., Portnyagin, A. S., Shits, E. Yu. (2017). Poluchenie sinteticheskih gidratov prirodnogo gaza iz l'da v zakrytyh reaktorah pri termociklirovanii. Nauka i obrazovanie, 3, 76–81.
21. Ganushevych, K., Sai, K., Korotkova, A. (2014). Creation of gas hydrates from mine methane. Progressive Technologies of Coal, Coalbed Methane, and Ores Mining, 505–509. doi: 10.1201/b17547-85
22. Bondarenko, V. I., Sai, K. S., Ganushevych, K. A. (2015). Mathematical model development of hydrate formation process intensification based on the results of experimental studies. Mining of Mineral Deposits, 9 (2), 259–266. doi: 10.15407/mining09.02.259
23. Bondarenko, V. I., Kharin, Ye. N., Antoshchenko, N. I., Gasyuk, R. L. (2013). Basic scientific positions of forecast of the dynamics of methane release when mining the gas bearing coal seams. Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, 5, 24–30.
24. Lozynskyi, V. H., Dychkovskyi, R. O., Falshtynskyi, V. S., Saik, P. B. (2015). Revisiting possibility to cross disjunctive geological faults by underground gasifier. Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, 4, 22–28.
25. Lozynskyi, V., Saik, P., Petlovanyi, M. (2018). Analytical research of the stress-deformed state in the rock massif around faulting. International Journal of Engineering Research in Africa, 35, 140–151.
26. Uddin, M., Wright, F., Dallimore, S., Coombe, D. (2014). Gas hydrate dissociations in Mallik hydrate bearing zones A, B, and C by depressurization: Effect of salinity and hydration number in hydrate dissociation. Journal of Natural Gas Science and Engineering, 21, 40–63. doi: 10.1016/j.jngse.2014.07.027
27. Bhade, P., Phirani, J. (2015). Effect of geological layers on hydrate dissociation in natural gas hydrate reservoirs. Journal of Natural Gas Science and Engineering, 26, 1549–1560. doi: 10.1016/ j.jngse.2015.05.016

28. Vadakkepuliyambatta, S., Chand, S., Bünz, S. (2017). The history and future trends of ocean warming-induced gas hydrate dissociation in the SW Barents Sea. Geophysical Research Letters, 44 (2), 835–844. doi: 10.1002/2016gl071841

29. Koltun, P., Klymenko, V. (2016). Methane Hydrates – Australian perspective. Mining of Mineral Deposits, 10 (4), 11–18. doi: 10.15407/mining10.04.011

30. Hanushevych, K., Srivastava, V. (2017). Coalbed methane: places of origin, perspectives of extraction, alternative methods of transportation with the use of gas hydrate and nanotechnologies. Mining of Mineral Deposits, 11 (3), 23–34. doi: 10.15407/mining11.03.023

31. Koh, C. A., Sum, A. K., Sloan, E. D. (2012). State of the art: Natural gas hydrates as a natural resource. Journal of Natural Gas Science and Engineering, 8, 132–138. doi: 10.1016/j.jngse.2012.01.005

32. Bondarenko, V. I., Ganushevich, K. A., Sai, E. S. (2011). K voprosu skvazhinnoy podzemnoy razrabotki gazovyh gidratov. Naukovyi visnyk NHU, 1, 60–66.

33. Bondarenko, V., Ganushevych, K., Sai, K., Tyshchenko, A. (2011). Development of gas hydrates in the Black sea. Technical and Geoinformational Systems in Mining, 55–59. doi: 10.1201/b11586-11

34. Lee, S. (2015). Marine gas hydrate – an indigenous resource of natural gas for Europe (MIGRATE): A marine gas hydrate project newly implemented in Europe. Journal of the Geological Society of Korea, 51 (5), 525. doi: 10.14770/jgsk.2015.51.5.525

35. Kozhevnikov, A. A., Sudakov, A. K., Dreus, A. Yu., Lysenko, Ye. Ye. (2013). Study of heat transfer in cryogenic gravel filter during its transportation along a drillhole. Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, 6, 49–54.

36. Mandryk, O., Pukish, A., Zelmanovych, A. (2017). Formation peculiarities of physical and chemical composition of highly mineralized edge water. Mining of Mineral Deposits, 11 (1), 72–79. doi: 10.15407/mining11.01.072

37. Kalacheva, L. P., Shits, E. Yu., Fedorova, A. F. (2009). Issledovanie mekhanohimicheskih prevrashcheniy gidratov prirodnogo gaza. Neftekhimiya, 49 (4), 310–314.

38. Kalacheva, L. P. (2013). Termodinamicheskiy analiz himicheskih prevrashcheniy komponentov prirodnogo gaza pri mekhanicheskoy obrabotke gazovyh gidratov. Tekhnicheskie nauki – ot teorii k praktike, 17-2, 37–41.

39. Gamolin, O. E. (2003). The transformation of natural gas structure under the influence of mechanical energy. The Genesis of Petroleum and Gas, 74.

40. Semyonov, M. E., Kalacheva, L. P., Shits, E. Y. (2014). Studying of features of processes of formation and mechano-chemical processing synthetic hydrates of natural ga. "Proceedings" of "OilGasScientificResearchProjects" Institute, SOCAR, 4, 40–45. doi: 10.5510/ogp20140400220

41. Weitemeyer, K. A., Constable, S., Tréhu, A. M. (2011). A marine electromagnetic survey to detect gas hydrate at Hydrate Ridge, Oregon. Geophysical Journal International, 187 (1), 45–62. doi: 10.1111/j.1365-246x.2011.05105.x

42. Vasyuk, B. N. (2015). Tendencii razvitiya tekhnologiy podvodnoy dobychi gaza iz zalezhey gazovyh gidratov. Porodorazrushayushchiy i metalloobrabatyvayushchiy instrument – tekhnika i tekhnologiya ego izgotovleniya i primeneniya, 18, 33–38.

43. Bondarenko, V., Maksymova, E., Koval, O. (2013). Genetic classification of gas hydrates deposits types by geologic-structural criteria. Mining of Mineral Deposits, 115–119. doi: 10.1201/b16354-21

44. Kalacheva, L. P., Rozhin, I. I., Fedorova, A. F. (2016). Izuchenie zavisimosti processov obrazovaniya i razlozheniya gidratov prirodnogo gaza ot himicheskoy prirody rastvorov elektrolitov, imitiruyushchih plastovye flyuidy. Mezhdunarodniy zhurnal prikladnyh i fundamental'nyh issledovaniy, 8-4, 565–569.

45. Kalacheva, L. P., Rozhin, I. I. (2017). The influence of the chloride-calcium-type water composition on the properties of natural gas hydrates. Neftegazovaya Geologiya. Teoriya i Praktika, 12 (3). doi: 10.17353/2070-5379/25_2017

46. Lang, X., Fan, S., Wang, Y. (2010). Intensification of methane and hydrogen storage in clathrate hydrate and future prospect. Journal of Natural Gas Chemistry, 19 (3), 203–209. doi: 10.1016/s1003-9953(09)60079-7

47. Holzammer, C., Finckenstein, A., Will, S., Braeuer, A. S. (2016). How Sodium Chloride Salt Inhibits the Formation of CO2 Gas Hydrates. The Journal of Physical Chemistry B, 120 (9), 2452–2459. doi: 10.1021/acs.jpcb.5b12487

48. Semenov, M. E., Shits, E. Yu. (2016). Izuchenie morfologii sinteticheskih gidratov prirodnogo gaza, poluchennyh iz l'da v ustanovkah zakrytogo tipa. Nauka-rastudent.ru, 10.

49. Aregbe, A. G. (2017). Gas Hydrate – Properties, Formation and Benefits. Open Journal of Yangtze Oil and Gas, 02 (01), 27–44. doi: 10.4236/ojogas.2017.21003

50. Giricheva, N. I., Ishchenko, A. A., Yusupov, V. I., Bagratashvili, V. N., Girichev, G. V. (2014). Struktura i energetika metanovyh gidratov. Izvestiya vysshih uchebnyh zavedeniy. Seriya: himiya i himicheskaya tekhnologiya, 57 (9), 3–9.

51. Ovchynnikov, M., Ganushevych, K., Sai, K. (2013). Methodology of gas hydrates formation from gaseous mixtures of various compositions. Mining of Mineral Deposits, 203–205. doi: 10.1201/b16354-37

52. 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, 123–127. doi: 10.1201/b19901-23

53. Bondarenko, V., Svietkina, O., Sai, K. (2017). Study of the formation mechanism of gas hydrates of methane in the presence of surface-active substances. Eastern-European Journal of Enterprise Technologies, 5 (6 (89)), 48–55. doi: 10.15587/1729-4061.2017.112313

54. Kuzmenko, O. M., Petlovanyi, M. V. (2015). Substantiation the expediency of fine gridding of cementing material during backfill works. Mining of Mineral Deposits, 9 (2), 183–190. doi: 10.15407/mining09.02.183

55. Svetkina, E. Yu., Petlevaniy, M. V. (2012). Zakonomernosti formirovaniya struktury i prochnosti tverdeyushchey zakladki pri raznoy dispersnosti vyazhushchego materiala. Zbirnyk naukovykh prats Natsionalnoho hirnychoho universytetu, 37, 80–87.

56. Opredelenie udel'noy poverhnosti poroshkov po soprotivleniyu fil'tracii razrezhennogo gaza. Metodika opredeleniya (1979). Moscow: AN SSSR, 6.

57. Kuz'menko, O., Petlyovanyy, M., Stupnik, M. (2013). The influence of fine particles of binding materials on the strength properties of hardening backfill. Mining of Mineral Deposits, 45–48. doi: 10.1201/b16354-10

58. Korsakov, V. G., Shelomenceva, I. V., Yur'evskaya, I. M., Petrova, L. I. (1983). Issledovanie energeticheskih harakteristik i prognozirovanie fiziko-himicheskih i tekhnicheskih svoystv materialov. Napravlenniy sintez tverdyh veshchestv, 1, 158–174.

59. Franchuk, V. P. (1995). Opredelenie temperatury v zone nagruzheniya pri vibroudarnom nagruzhenii. Teoriya i praktika processov izmel'cheniya i razdeleniya, 15–23.

60. Franchuk, V. P. (2010). Vibracionnaya tekhnika v malyh proizvodstvah. Heotekhnichna mekhanika, 85, 290–296.

61. Svetkina, O. (2013). Receipt of coagulant of water treatment from radio-active elements. Mining of Mineral Deposits, 227–230. doi: 10.1201/b16354-42

62. Grauls, D. (2001). Gas hydrates: importance and applications in petroleum exploration. Marine and Petroleum Geology, 18 (4), 519–523. doi: 10.1016/s0264-8172(00)00075-1

63. Ganushevych, K., Sai, K. (2013). Development of gas hydrate reservoir in the Black Sea. Young Petro, 8, 45–50.

64. Sai, K. S. (2016). Obgruntuvannia parametriv tekhnolohiyi rozrobky hazohidratnykh pokladiv neodnoridnoi struktury. Dnipro: NHU, 203.

65. Svetkina, Ye. Yu. (2013). Intensification of concentration process through minerals vibroactivation. Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, 2, 38–43.

66. Svetkina, Y., Falshtyns'kyy, V., Dychkovs'kyy, R. (2010). Features of selectivity process of borehole underground coal gasification. New Techniques and Technologies in Mining, 219–222. doi: 10.1201/b11329-37

67. Say, E. S., Svetkina, E. Yu. (2012). Izuchenie processov diffuzii pri razrabotke gazogidratnyh zalezhey. Materialy V mezhdunarodnoy konferencii «Shkola podzemnoy razrabotki», 201–206.