

KINETIC FEATURES OF THE DISSOCIATION PROCESS OF GAS HYDRATE DEPOSITS

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Abstract. *The research is aimed at revealing the theoretical features of the kinetics of the process of dissociation of natural gas hydrates, the accounting of which is useful in designing technologies for their development. The process of decomposition of gas hydrates is considered as a heterogeneous process, proceeding at the interface of the phases and contains three consecutive stages. The mathematically grounded speed with which molecules fluctuate around fixed positions and the velocity of their translational motion in the system “gas – rock environment”. The mathematical expression of the constant coefficient of molecular diffusion is made. It has been established that when gas is extracted from gas hydrates, external and internal diffusion zones, as well as diffusion inhibition, are caused, which causes an increase in the decay time of gas hydrate to gas and water. The character of the dependence of the change in the rate of dissociation during its various periods is revealed. It was found that the speed of the dissociation process in these conditions varies with the temperature under the exponential law.*

Keywords: *gas hydrate, dissociation, mining, fuel, thermobaric conditions.*

Introduction. In today's fast-moving conditions of intensive energy consumption, it is obvious that in the near future, mankind will exhaust most of the discovered natural gas deposits [1, 2]. In this regard, the international scientific community is actively conducting research on the possibility of using alternative types of fuel and searching for additional sources of energy [3 – 5]. To date, there is no alternative energy source that can significantly reduce the impact of traditional fossil fuels to ensure the energy independence of modern states. The future development of the energy sector of Ukraine is directly related to a sufficient level of production as solid combustible minerals in various ways. [6 – 9], as hydrocarbons [10 – 13], in the development of which there is no industrial waste [14, 15]. A promising direction in the development of hydrocarbon sources is the development of gas hydrate deposits, which are currently being mined in a number of developed countries [16 – 18], and in Ukraine only at the level of theoretical study [19, 20]. For Ukraine, the gas hydrate deposits of the Black Sea are of considerable interest, since the gas reserves concentrated in the Ukrainian part (20 – 25 trillion m³) exceed several times the existing gas reserves of traditional deposits, which will allow Ukraine to provide this energy supply for several centuries, taking into account all necessary needs of both the industrial complex of the state and the population [21 – 23].

As a result of a comprehensive analysis and systematization of existing data on the patterns of hydrate formation and hydrate accumulation under natural conditions, it was found that gas hydrate deposits are deposited not only with continuous layers of pure gas hydrate, but contain a certain proportion of rock inclusions [24, 25], what should be considered when studying the kinetics of the process of its dissociation and the development of technological schemes of production.

Thus, the establishment of the kinetic features of the decomposition process of natural gas hydrates and the determination of their mechanism is a pressing issue in the development of technologies for the integrated development of gas hydrate deposits as an alternative source of energy.

Research results. The process of decomposition of gas hydrates, like any other heterogeneous process, proceeds at the interface of the phases and contains three consecutive steps (phases):

- the first stage involves the transfer of heat to the surface of the solid phase – the reaction zone – in which the transition of one structure of hydrated ice to another, as well as its melting;
- the second stage is the dehydration of the gas hydrate, that is, the adsorption-chemical act on the surface of the section;
- the third stage consists in the complete dissociation of the gas hydrate and the removal of the reaction products (methane gas and water) from the reaction zone.

The main stages of decomposition of a gas hydrate deposit of an inhomogeneous structure containing a certain proportion of rock inclusions are given in Figure 1.

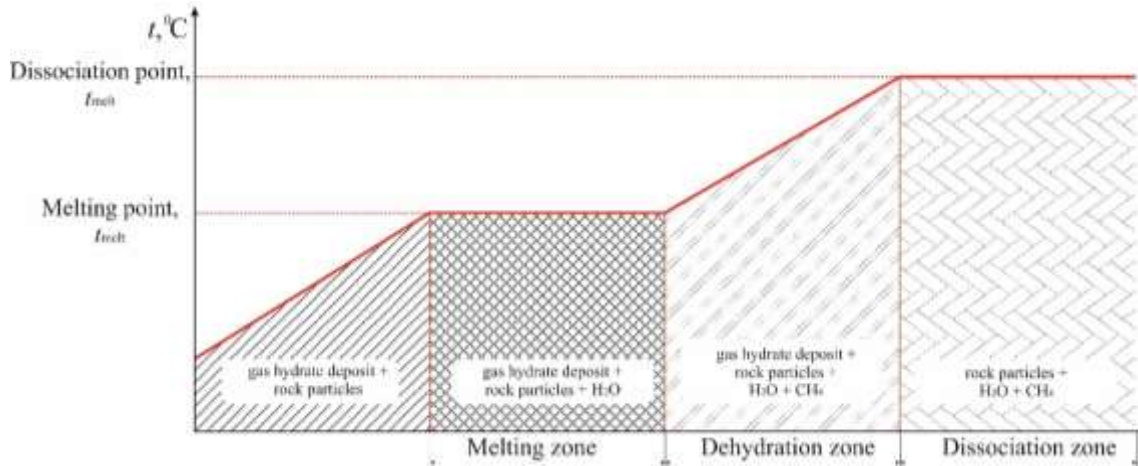


Fig. 1. Formation of the stages of decomposition of the gas hydrate deposit of the inhomogeneous structure

At the first stage melting of the gas hydrate deposit, where there is a partial separation of water from the deposit. In this case, two aggregate states of substances that take place in the structure of the inhomogeneous structure can be singled out: gas hydrate and rock inclusions, which are solids, and water, which is a liquid. The second stage involves the process of dehydration. There is a partial decomposition of methane gas molecules, the third aggregate state of matter is gaseous, but the gas output is not maximal, since the thermal state of the gas hydrate deposit of the inhomogeneous structure does not reach the limiting point, for the introduced energy, at which there is a transition to the dissociation zone. The process of dissociation is the third stage in which there is a full factor separation of methane gas, the allocation of water and the isolation of rock inclusions.

The process of decomposition of gas hydrates occurs as a result of the shift of thermobaric parameters of their stable existence, that is, the molecules of gas, released from the cavities of clathrate, may be delayed in or through the volume of ice or soil. Thus, the penetration of the active zone to a greater depth is observed [17, 26, 27], which leads to bulk ionization of the activated material.

Brownian's motion of gas and liquid particles in the process of passing through the soil is usually not taken into account, since the pathway of particles passing through Brownian's diffusion of about 0.1 microns is not more than 5% (often no more than 1–2%), and particles of 1 microns or more are less 1% of the average path of the volume flow of liquid during passage through porous materials. Another picture is observed at the passage of gaseous substances, when the diffusion component is one of the main in the mechanism. In the development of gas hydrate deposits there is a change in temperature regime, which leads to thermal motion as a liquid, which is a by-product of dissociated gas hydrate, and gas, therefore, it is necessary to take Brownian's motion into account [28].

To do this, consider the equation of the linear motion of particles of mass m , on which the constant force F and the resistance is proportional to the velocity:

$$m \frac{d^2 x}{dt^2} = F - \frac{dx}{dt}.$$

The solution, averaged over all the particles in the system, has the form:

$$x^2 = \frac{2kTt}{C} \left\{ 1 - \frac{m}{Ct} \left[1 - \exp\left(-\frac{Ct}{m}\right) \right] \right\} = 2Dt \left\{ 1 - \frac{mD}{kTt} \left[1 - \exp\left(-\frac{kTt}{mD}\right) \right] \right\}, \quad (1)$$

where $D = \frac{kT}{C}$ – coefficient of diffusion; C – coefficient of resistance.

In comparison with the usual molecule, the gas hydrate is a macromolecule that moves according to the laws established for Brownian particles. Therefore, the distance traversed by it in any direction will not be proportional to the travel time, as in the case of a body whose vector of velocity remains constant. The chaotic (disordered) motion is characterized by another pattern: the mean square of the distance to which the particle moves over time is proportional to the absolute temperature and inversely proportional to the particle coefficient of friction. Already after a short time interval (for particles with a molecular weight

of 40 g/moles in water at room temperature, the time interval is approximately $2 \cdot 10^{-12}$ s), the value will be up to 90% of the limit. For longer time intervals the equation will look like:

$$x^2 = 2Dt .$$

This equation characterizes the important property of the diffusion process: the time required for diffusion increases proportionally to the square of the distance. The diffusion coefficient will be determined by the size and shape of the molecules. The particle is in a constant zigzag movement, which is caused by chaotic collisions with other gas molecules and a viscous environmental resistance that is characteristic of secondary gas hydrate deposits.

However, if we consider the motion for less than $2 \cdot 10^{-12}$ s, then, as can be seen from equation (1), the motion becomes independent of viscosity (primary gas hydrate deposits). These are leaps forward and back with frequency order of oscillatory frequencies:

$$v = \frac{1}{2\Delta} \left(\frac{kT}{m} \right)^{\frac{1}{2}},$$

where $\Delta = \left(\overline{x^2} \right)^{\frac{1}{2}}$.

Thus, the velocity with which the molecules fluctuate around the fixed positions and the velocity of their translational motion in the “gas – rock environment” system, which consists of liquid and gaseous parts, is obtained.

Passage of gases through the environment includes the following cases:

- penetration through the pores;
- penetration through holes cracks;
- full plugging of the mouth of the channel.

In Figure 2 schematically depicts the flow of gas through an environment consisting of mineral particles of the rock bottom sediments.

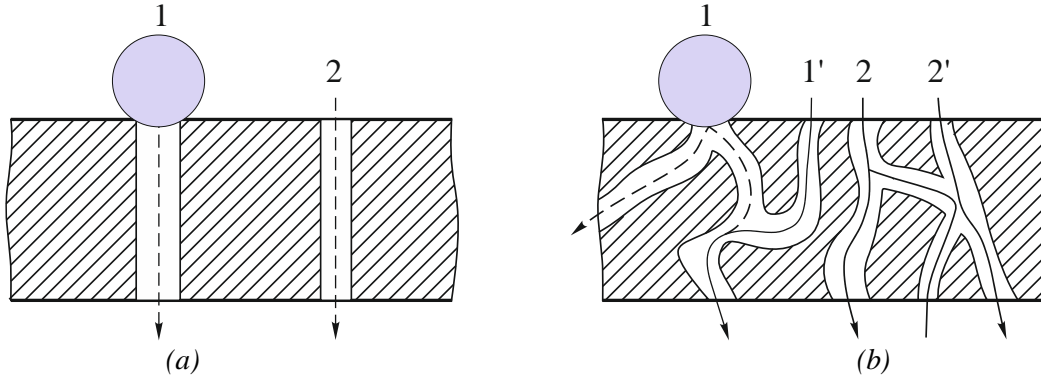


Fig. 2. Scheme of gas flow and clogging capillaries in the ideal (a) and real (b) systems

For an ideal system, the blockage of the mouth of one of the channels (Fig. 2a, 1) leads to the cessation of movement of fluid in it. The labyrinth system of interconnected channels provides, when the main mouth of the main canal is hammered (Fig. 2b), the detection and disclosure of the side (Fig. 2b, 1') with a mouth of smaller or larger diameter. As a result of the opening of the side channels, there is a partial compensation for the drop in permeability when the main channel's mouth is clogged.

When considering the diffusion component in the process of extracting gas from the gas hydrate layers of the inhomogeneous structure, it is necessary to isolate the outer and inner regions of diffusion. The intrinsic diffusion region of the process flow in turn can be divided into two sections, which are determined by the ratio $\frac{2r}{\lambda}$, where λ – length of free run of the molecule, and r – pore radius:

1. The Knudsen's diffusion region corresponds to inequality $\frac{2r}{\lambda} < 1$. Consequently, the free path of the molecule is greater than the average pore size.

2. The area of molecular diffusion within the pores corresponds to inequality $\frac{2r}{\lambda} > 1$. In this case, the probability of collisions between molecules is greater than with the walls of pores. In this case, the diffusion coefficient does not depend on the pore size, but is related to the length of the free run of the molecules.

Thus, when the average mileage of a molecule in the gas phase is large in comparison with the radius of the pore, the diffusion coefficient is determined by the flow of Knudsen; if so $\lambda < 2r$, then there is molecular diffusion.

The general equation for determining the effective diffusion coefficient, which shows the relation between the diffusion of Knudsen and ordinary diffusion, is written as follows:

$$D_k = \frac{1}{3} \bar{u} \lambda \left(\frac{2r\lambda}{1 + 2r/\lambda} \right),$$

where \bar{u} – average Maxwell's speed equal to:

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}}, \quad (2)$$

where R – universal gas constant; T – temperature; M – molecular weight.

Formula (2) should be used with adherence r and λ .

At a pressure of 0.1 MPa (1 atm) for a pore size of 50 nm or more there is a complete transition to molecular diffusion, and the diffusion coefficient becomes constant. This corresponds to the following expression:

$$D = \frac{1}{3P} \left(1 - e^{-2 \cdot 10^5 r P} \right).$$

With the dissociation of the gas hydrate, diffusion inhibitory increases the time of its decomposition into methane and water. The rate of decomposition of the gas hydrate decreases with increasing depth of transformation due to diffusion inhibition. The decrease begins in the transition region and reaches the largest value in the area of internal diffusion, after which it remains constant.

The boundary of domains in diffusion braking in the process of decomposition of gas hydrate is more rational expressed through the hydraulic radius r_{hydr} , which is in the area of diffusion of Knudsen $\frac{2r_{hydr}}{\lambda} < 1$, but in the field of molecular diffusion $\frac{r_{hydr}}{\lambda} > 1$. On average, for these systems $r_{hydr} \approx \frac{r}{2}$.

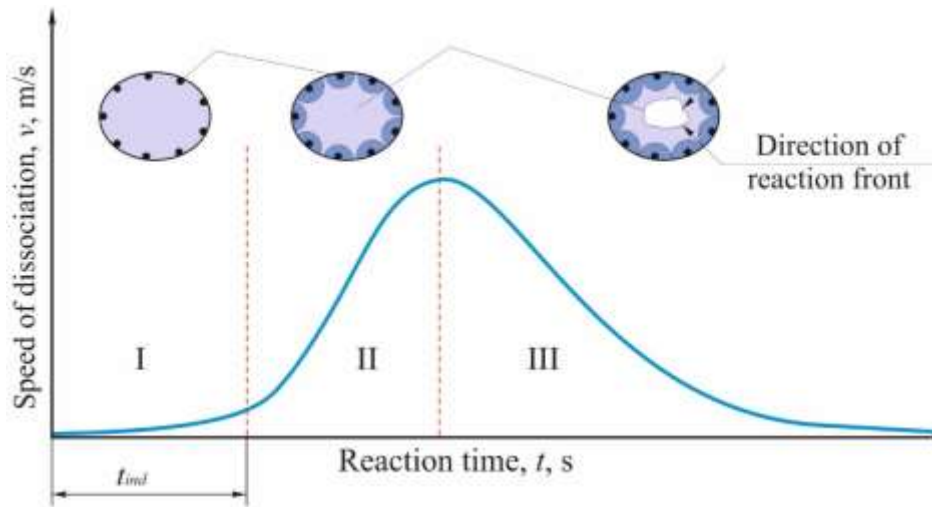
Proceeding from the foregoing, the support of the diffusion and kinetic stages is comparable, so the interaction mode is mixed. It is important that any of the stages did not limit the speed of the process in a permanent (stationary) mode, the speed of all stages is the same. Let's consider the kinetics of the heterogeneous process of decomposition of gas hydrates of an inhomogeneous structure.

The process of dissociation of gas hydrate $M \cdot nH_2O + \Delta H \rightarrow M + nH_2O$ is heterogeneous, since it occurs at the interface between the solid phase - the starting gas hydrate and a mixture of liquid and gas. The process of dissociation is a topochemical process, which is accompanied by the disappearance of one phase by the transition of hydrated ice to a more fragile structure and, finally, the emergence of new phases. This transition is accompanied by the formation of a new and destruction of the old crystal lattice. This stage takes some time and is characterized by an induction period, that is, the process is auto-catalytic, and it is during this period that the dissociation reaction proceeds at a negligible low speed.

The beginning of the decomposition process is initiated by the formation of a certain number of cavities in hydrated ice that is sufficient for the actual restructuring of its structure, which is necessarily due to the presence of the required energy reserve, due to which separation of molecules of gas from water molecules occurs. The emergence of the nuclei of a new phase and, consequently, the surface of the separation between the two solid phases (gas hydrate and rock inclusions), as well as the dissociation of the gas hydrate deposit of the inhomogeneous structure, are already on the surface of solid inclusions represented by aluminosilicates.

The boundary between the solid phase gradually moves inside the crystal lattice of the maternal phase from the moment of the emergence of a new phase, which occurs in the expansion of the deposit.

It should be noted that increasing the degree of dispersion of rock inclusions leads to an increase in the number of active centers, which are the peaks of rock crystals, some defective spots on their faces and edges, where the particles of matter have an increased supply of energy. The growth of the number of active centers leads to a decrease in the induction period (Fig. 3, period I).



I – induction period (the reaction proceeds at an extremely low speed); II – autocatalytic period (noticeable increase in the reaction rate due to the growth of the interface between the solids); III – the period completion of the reaction (the speed falls due to the reduction of the reaction front)
 Fig. 3. Dependence of velocity (v) topochemical response on time (t)

The increase of the interphase boundary facilitates the further course of the dissociation reaction, which leads to an increase in the amount of gas hydrate per unit time, that is, the reaction rate (Fig. 3, period II). Finally, the surface of the solid phase separation, reaching its maximum value, begins to decrease due to the fact that the solid gas hydrate deposit has finite dimensions and, hence, the final value of the surface area (Fig. 3, period III). Simultaneously with the decrease of the boundary of the solid phase, the process speed drops. The decrease of speed contributes to the growth of the surface of the rock. If its porosity is small, then the process eventually passes into the diffusion regime, and the limiting step becomes the diffusion of gas molecules from the reaction zone. With a considerable porosity and relatively small dimensions of the dissociation phase, the kinetic mode of the process (the slowdown of the transformation) will be maintained.

In other words, the constant of the diffusion rate $K_{dif} = \frac{D}{\delta}$ in the expression for the rate of heterogeneous reaction $v = \frac{P_{O_2}}{\frac{\delta}{D} + \frac{1}{k}}$ will turn out to be larger compared to the constant of adsorption-chemical interaction k . The process speed in these conditions varies with the temperature according to the exponential law:

$$V = A \cdot \exp\left(\frac{-E}{RT}\right),$$

where A – complex function, which depends on the composition of the gas phase, the size and nature of the surface of the solid phase, the presence of impurities in it, and the like; E is the activation energy (the minimum value of the kinetic energy with which the particles move to each other is necessary in order for the meeting to be effective (calculated for one single element of the elementary acts)).

Thus, analytical studies of the kinetic features and mechanism of the decomposition process of natural gas hydrates will be useful when conducting experimental laboratory studies to clarify the decomposition time in various temperature and pressure conditions, which must be considered when developing technologies for the production of gas hydrates.

Conclusions. The kinetic peculiarities of the process of decomposition of gas hydrate layers of inhomogeneous structure, which takes place when the thermobaric parameters of their stable existence

are shifted, are considered. It has been established that when gas is extracted from gas hydrates, external and internal diffusion zones, as well as diffusion inhibition, are caused, which causes an increase in the decay time of gas hydrate to gas and water.

REFERENCES

1. *Resources to reserves 2013 – oil, gas and coal technologies for the energy markets of the future.* (2013). Paris: International Energy Agency.
2. Statistical review of World energy. (2015). London: Centre for Energy Economics Research and Policy, Pureprint Group Limited.
3. Adhikari, D. (2018). Solar energy as an alternative source of energy. *Bibechana*, (2), 1-7. <https://doi.org/10.3126/bibechana.v2i0.19227>
4. Hepbasli, A. (2004). Oil shale as an alternative energy source. *Energy Sources*, 26(2), 107-118. <https://doi.org/10.1080/00908310490258489>
5. Mykhailov, V. (2016). Prospection and estimation of unconventional hydrocarbon deposits in Ukraine. *Visnyk of Taras Shevchenko National University of Kyiv. Geology*, 2(73), 38-45. <https://doi.org/10.17721/1728-2713.73.06>
6. Petlovanyi, M.V., Lozynskiy, V.H., Saik, P.B., & Sai, K.S. (2018). Modern experience of low-coal seams underground mining in Ukraine. *International Journal of Mining Science and Technology*, 28(6), 917-923. <https://doi.org/10.1016/j.ijmst.2018.05.014>
7. Saik, P., Petlovanyi, M., Lozynskiy, V., Sai, K., & Merzlikin, A. (2018). Innovative approach to the integrated use of energy resources of underground coal gasification. *Solid State Phenomena*, (277), 221-231. <https://doi.org/10.4028/www.scientific.net/ssp.277.221>
8. Lozynskiy, V., Saik, P., Petlovanyi, M., Sai, K., Malanchuk, Z., & Malanchuk, Y. (2018). Substantiation into mass and heat balance for underground coal gasification in faulting zones. *Inzynieria Mineralna*, 19(2), 289-300. <https://doi.org/10.29227/IM-2018-02-36>
9. Хорольський, А., Грінюв, В., & Мамайкін, О. (2019). Інноваційні перспективи підземної експлуатації вугільних родовищ. *Вісник Житомирського державного технологічного університету. Серія: Технічні науки*, 1(83), 289-298. [https://doi.org/10.26642/tn-2019-1\(83\)-289-298](https://doi.org/10.26642/tn-2019-1(83)-289-298)
10. Bondarenko, V., Maksymova, E., Ganushevych, K., & Sai, K. (2013). Gas hydrate deposits of the Black Sea's trough: currency and features of development. *Szkola Eksploatacji Podziemnej: materiały konferencyjne* (pp. 66-69). Krakow: Instytut Gospodarki Surowcami Mineralnymi i Energią, Akademia Górniczo-Hutnicza.
11. Sai, K., Petlovanyi, M., Lozynskiy, V., & Saik, P. (2018). Economic efficiency of methane extract from gas hydrates deposits of heterogeneous structure. *Journal of Donetsk Mining Institute*, (2), 7-17. <https://doi.org/10.31474/1999-981x-2018-2-7-17>
12. Natural gas production. (2013). *Oil and Energy Trends*, 38(1), 24-26. https://doi.org/10.1111/oet.12037_4
13. Pedchenko, M., Pedchenko, L. (2016). Technological complex for production, transportation and storage of gas from the offshore gas and gas hydrates fields. *Mining of Mineral Deposits*, 10(3), 20-30. <https://doi.org/10.15407/mining10.03.020>
14. Popovych, V., Kuzmenko, O., Voloshchyshyn, A., & Petlovanyi, M. (2018). Influence of man-made edaphotopes of the spoil heap on biota. *E3S Web of Conferences*, (60), 00010. <https://doi.org/10.1051/e3sconf/20186000010>
15. Petlovanyi, M.V., & Medianyk, V.Y. (2018). Assessment of coal mine waste dumps development priority. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu*, (4), 28-35. <https://doi.org/10.29202/nvngu/2018-4/3>
16. 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. <https://doi.org/10.1016/j.jngse.2014.07.027>
17. 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. <https://doi.org/10.1016/j.jngse.2015.05.016>
18. Max, M.D., & Johnson, A.H. (2016). Commercial potential of natural gas hydrate. *Exploration and Production of Oceanic Natural Gas Hydrate*, 355-394. https://doi.org/10.1007/978-3-319-43385-1_11
19. Bondarenko, V., Ganushevych, K., Sai, K., & Tyschenko, A. (2011). Development of gas hydrates in the Black sea. *Technical and Geoinformational Systems in Mining*, 55-59. <https://doi.org/10.1201/b11586-11>
20. Bondarenko, V., Ganushevych, K., & Sai, K. (2012). Substantiation of technological parameters of methane extraction from the Black Sea gas hydrate. *Szkola Eksploatacji Podziemnej: materiały konferencyjne* (pp. 191-196). Krakow: Instytut Gospodarki Surowcami Mineralnymi i Energią, Akademia Górniczo-Hutnicza.

21. Korsakov, O.D., Stupak, S.N., & Byakov, Yu.A. (1991). Black Sea gas hydrates are an unconventional type of hydrocarbon raw. *Geologicheskii Zhurnal*, (5), 67-75.
22. Merey, S., & Sinayuc, C. (2016). Analysis of the Black Sea gas hydrates. *International Journal of Chemical and Molecular Engineering*, 10(8), 985-993.
23. Makogon, Y.F., Holditch, S.A., & Makogon, T.Y. (2007). Natural gas-hydrates – a potential energy source for the 21st century. *Journal of Petroleum Science and Engineering*, 56(1-3), 14-31. <https://doi.org/10.1016/j.petrol.2005.10.009>
24. Bondarenko, V., Sai, K., Ganushevych, K., & Ovchynnikov, M. (2015). The results of gas hydrates process research in porous media. *New Developments in Mining Engineering 2015: Theoretical and Practical Solutions of Mineral Resources Mining*, 123-127. <https://doi.org/10.1201/b19901-23>
25. Bondarenko, V.I., & Sai, K.S. (2018). Process pattern of heterogeneous gas hydrate deposits dissociation. *Naukovi Visnyk Natsionalnoho Hirnychoho Universytetu*, (2), 21-28. <https://doi.org/10.29202/nvngu/2018-2/4>
26. 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. <https://doi.org/10.15407/mining09.02.183>
27. Петлеваный, М.В., Кузьменко, А.М., Горобец, Л.Ж., Прядко, Н.С., & Усатый, В.Ю. (2011). О механической активации компонентов твердеющей закладки для заполнения выработанного пространства рудников. *Металлургическая и горнорудная промышленность*, (3), 75-78.
28. Bondarenko, V., Sai, K., Prokopenko, K., & Zhuravlov, D. (2018). Thermodynamic and geomechanical processes research in the development of gas hydrate deposits in the conditions of the Black Sea. *Mining of Mineral Deposits*, 12(2), 104-115. <https://doi.org/10.15407/mining12.02.104>