

ADSORBED METHANE DISPLACEMENT BY WATER VAPOUR INTO CLOSED CAVITY OF COAL-ROCK SEAMS

¹Stefanovych L.I., ¹Feldman E.P., ²Mazur O.Yu.

¹Branch for Physics of Mining Processes of the M.S. Poliakov Institute of Geotechnical Mechanics of the NAS of Ukraine, ²Technical University of Liberec

Abstract. In gas-saturated coal mass, closed cracks and pores, in addition to free methane, contain methane, which is associated with adsorption centers on their internal surfaces. It is known that as a result of ingress of moisture in the form of water vapor into these cavities, adsorbed methane tends to pass from the adsorption layer into the gaseous phase. The purpose of this work is to find out how significant the increase in the pressure of gaseous methane in the closed cavities of the coal matrix is due to its desorption from the inner surface of the pores and/or cracks as a result of the penetration of moisture into them in the form of water vapor. The problem is solved under the assumption that an increase in the partial pressure of water vapor inside cracks and pores occurs as a result of filtration phenomena, i.e. relatively slowly compared to the adsorption-desorption processes occurring on the inner surfaces of the voids of the coal substance.

When calculating the excess partial pressure of methane, which arose as a result of its displacement from the adsorption layer by water molecules, the Langmuir approximation was used for the degrees of coverage of the adsorption layer by methane and water molecules, i.e. single-layer adsorption approximation. It is shown that in the case of macroscopic cavities of the order of 10^{-3} m and more, this phenomenon is insignificant. However, for gas-filled closed cavities with a size of the order of micrometers or less and with an initial pressure of gaseous methane of the order of 1 MPa, the relative excess pressure of gaseous methane as a result of its desorption from the inner surface of closed cracks and pores can be tens of percent.

The scientific novelty of the work lies in the fact that, as far as the authors know, calculations related to the appearance of excess pressure of methane in closed cracks and pores as a result of its displacement by water vapor from the inner surface of closed voids of the coal matrix have not been carried out before. An increase in the pressure of gaseous methane inside closed cavities can lead to an increase in their size, in particular, this applies to cracks that are located near macroscopic voids.

Keywords: gas-filled cracks and pores, excess gaseous methane, desorption, inner surface of cavities, water vapor.

1. Introduction

A characteristic feature of most rocks including coal is their heterogeneous structure, due to the presence of various kinds of cavities in them, such as, pores, cracks and filtration channels. These cavities, as a rule, are filled with mine gases (mainly methane and water vapor), which are under some pressure. Due to the presence of a certain number of active adsorption centers N_a , gases in the cavities of coal can be not only in a free state, but can be adsorbed on the inner surfaces of cracks and pores, forming the so-called adsorption layer. In the absence of external influences, these states of methane are in thermodynamic equilibrium. In this case, the coverage rate of the adsorption layer by methane molecules and the pressure of the gas phase remain unchanged. Thus, gas adsorption/desorption can be considered as one of the factors for the generation of gas outbursts. Thus, in the theoretical work [1], gas desorption caused by excessive stress is identified as a key factor, which is responsible for the increase in pore pressure near the working surface, and is associated with an increase in stress level, evolution of permeability and drainage conditions during the start of outbursts. However, in our opinion, another important factor in the desorption of me-

thane from the inner surface of cavities and its transition to a gaseous state is the penetration of water vapor into gas-filled cracks and pores due to coal moistening.

The effect of coal moisture on the sorption properties was experimentally studied in many works [2–7], in which were shown that coal moistening always leads to a decrease in its sorption methane capacity. As for theoretical studies, the results of these works are quite contradictory. For example, the traditional approach to modeling does not take into account the competitive adsorption between the adsorbed gas and water in coal [3].

However, the ratio between the sorbed and gaseous components of methane in closed small cavities of coal during its moistening can change upon water vapor penetrating into gas-filled cracks and pores. The penetration of water vapor into cracks and pores can occur by filtration processes through a network of small filtration channels. Such phenomena can occur, for example, when the groundwater level rises upon flooding the mines. One of the technological solutions to reduce the influx of methane into the production face is the purposeful wetting of the coal seam by injecting water through wells drilled from the earth's surface or from underground workings. Water vapor penetration into closed cavities can also occur during shale gas fracturing as a side effect. Thus, the study of the processes of methane desorption from the inner surfaces of closed cracks and pores under the influence of water vapor penetrating into them remains relevant.

The theoretical analysis of the effect of water vapor on methane desorption from the surface of open cracks and pores was carried out previously by the authors of current paper [8]. However, in practical issues, the study of the effect of water vapor on the increase of pressure in gas phase inside the closed cracks and pores seems more important. Therefore, in this study, the task is to find out how significant the increase of the pressure in the gas phase in closed cavities of the coal matrix will be due to its desorption from the inner surface of the pores and/or cracks upon the coal substance moistening.

2. Methods

Let us consider a closed cavity inside a coal matrix containing methane and water vapor. The further consideration we are doing as before [8] in the Langmuir approximation. In this case it is assumed that the adsorption layer of methane inside the cavities of the coal substance is monomolecular, and its temperature coincides with the temperature of the coal substance and the temperature of the gas inside the cavity. For definiteness, we assume that this temperature T is about 300 K. If the pressure of gaseous methane inside the cavity at the initial moment of time is $p_1^{(0)}$, (MPa) and the pressure of the water vapor is $p_2^{(0)}$, (MPa) then in the state of thermodynamic equilibrium, the coverage rate of the adsorption layer by methane molecules is

$$g_1^{(0)} = \frac{p_1^{(0)} f_1}{1 + p_1^{(0)} f_1 + p_2^{(0)} f_2}, \text{ (dimensionless coefficient) } (1)$$

where the expressions

$$f_1 = p_{1,T}^{-1} \exp(u_1/RT), (MPa^{-1}); \quad f_2 = p_{2,T}^{-1} \exp(u_2/RT), (MPa^{-1}) \quad (2)$$

depend on the temperature of the adsorption layer T , (K) only. Here $R, kJ/(K \cdot mol)$, is a universal gas constant; $p_{1,T}, (MPa)$ and $p_{2,T}, (MPa)$ are saturated vapor pressures of methane and water, respectively, at a temperature T , (K); $u_1, (kJ)$ and $u_2, (kJ)$ are absolute values of the binding energies of methane and water molecules with coal substance. As is known, the methane and water molecules are prone to adsorption on the surface of a coal substance. Therefore, their binding energies (more precisely, the difference between the energies of molecules in the adsorption layer and in the gas phase $u_i = u_i^S - u_i^g, (kJ)$, $i = 1, 2$.) have a negative sign $u_1 < 0$, $u_2 < 0$. Experimental magnitudes of binding energies of methane and water molecules with a surface of the coal substance show the fulfillment of the ratio [7]

$$|u_2| > |u_1|, (kJ). \quad (3)$$

The expression for the equilibrium coverage rate of the inner surface of the cavity with water molecules has a similar form $g_2^{(0)}$ (dimensionless coefficient)

$$g_2^{(0)} = \frac{p_2^{(0)} f_2}{1 + p_1^{(0)} f_1 + p_2^{(0)} f_2}. \text{ (dimensionless coefficient)} \quad (4)$$

Let us consider what will happen in the process of moistening the coal seam and penetration by filtering water vapor molecules into cracks and pores. In this case, water molecules, penetrating into cracks and pores, change the water vapor pressure above the adsorption layer. Thus, they violate the conditions of dynamic equilibrium that were observed before water entered the coal seam. We emphasize that we do not talk about moisture in a condensed state, but about that part of it that continues to remain in the coal in the form of water vapor.

3. Theoretical part

We assume that the partial pressure of water vapor inside the cavity has a value $p_2^{(0)}, (MPa)$ at the initial moment of time. Let us analyze the situation when, at some point in time, the water vapor penetrated from the outside into a closed cavity inside the coal matrix, for example, due to filtration processes. Then, over time, the vapor pressure inside the cavity increases, i.e. becomes a function of time $p_2(t) = p_2^{(0)} + \Delta p_2(t), (MPa)$.

Considering that between the binding energies of methane and vapor molecules the relation (3) is satisfied, then the part of methane molecules from the adsorption

layer starts to displace by water molecules into the volume of the cavity, so that the coverage rate of the adsorption layer by methane molecules becomes less. If the cavity is closed, then due to the desorbed methane, the pressure of gaseous methane inside the cavity increases. Consequently, the pressure of gaseous methane inside the cavity becomes a function of time $p_1(t) = p_1^{(0)} + \Delta p_1(t)$, (MPa).

At low pressures, the gaseous methane in the cavity can be considered as an ideal gas. Then a simple geometric consideration, taking into account the equation of state of the gas $\Delta p_1 V = \Delta \mathcal{G}_1 N_a T$, shows that the rate of change in pressure of gaseous methane, due to its desorption from the inner surface of the cavity, turns out to be equal to $\partial p_1 / \partial \mathcal{G}_1 = -(T / r \sigma_m)$, where $\sigma_m, (nm^2)$ is the area per one adsorption center on the surface, r is the ratio of the volume of the cavity to its surface area. In the case of a crack, this is its gaping z , (m) and in the case of a pore, we have $r = r_p / 3$, (m) where r_p , (m) is just its radius. Here we measure temperature T in energy units (kJ). It follows from physical considerations that the excess pressure of gaseous methane inside the cavity, due to desorption, is proportional to the decrease in the coverage rate of the adsorption layer by methane molecules

$$\gamma \Delta p_1(t) = \gamma (p_1(t) - p_1^{(0)}) = \mathcal{G}_1^{(0)} - \mathcal{G}_1(t). \quad (5)$$

Here $\mathcal{G}_1(t)$ (dimensionless coefficient) is the degree of filling the inner surface of the cavity with adsorbed methane at the time t , and coefficient γ in general case is determined as $\gamma = (\partial p / \partial \mathcal{G}_1)^{-1} = (r \sigma_m / T)$, where $\sigma_m, (nm^2)$ is the area per one sorbed methane molecule. Considering a pore as a cavity, we obtain the expression for the parameter $\gamma_p = \partial p / \partial \mathcal{G}_1)^{-1} = (r_p \sigma_m / 3T)$. For a crack it is $\gamma_{cr} = (\partial p / \partial \mathcal{G}_1)^{-1} = (z \sigma_m / T)$. We assume that the process of changing the pressure of water vapor $p_2(t)$ in a closed cavity occurs due to the filtration of moisture from the surrounding carbon matrix. Then it proceeds rather slowly (quasi-statically) compare to the adsorption-desorption processes inside the cavity. In this approximation, the change in the coverage rate of the adsorption layer by methane molecules $\mathcal{G}_1(t)$, can be described by a function of the form (1), where it should be taken into account that the pressures of methane $p_1(t)$, (MPa) and water $p_2(t)$, (MPa) vapor are functions depending on time

$$\mathcal{G}_1(t) = \frac{(p_1^{(0)} + \Delta p_1(t)) f_1}{1 + (p_1^{(0)} + \Delta p_1(t)) f_1 + (p_2^{(0)} + \Delta p_2(t)) f_2}. \quad (\text{dimensionless coefficient}) \quad (6)$$

The substitution of the expressions (6) and (1) into the equality (5) gives an equation

$$\gamma \Delta p_1(t) = \frac{p_1^{(0)} f_1}{1 + p_1^{(0)} f_1 + p_2^{(0)} f_2} - \frac{(p_1^{(0)} + \Delta p_1(t)) f_1}{1 + (p_1^{(0)} + \Delta p_1(t)) f_1 + (p_2^{(0)} + \Delta p_2(t)) f_2}. \quad (7)$$

Here, the initial partial pressures of methane and water inside the closed cavity, must be set as $p_1^{(0)}$, (MPa) and $p_2^{(0)}$ (MPa) respectively, and the desired pressure here is the excess pressure of methane $\Delta p_1(t)$, due to its desorption from the inner surface of the cavity. The transformation of the equation (7) shows that we are dealing with a quadratic equation of the form

$$a(\Delta p_1(t))^2 + b(\Delta p_1(t)) - c = 0, \quad (8)$$

where the coefficients of the equation are determined by the following relations:

$$a = \gamma f_1(1 + p_1^{(0)} f_1 + p_1^{(0)} f_2), \text{ (MPa}^{-2}\text{)} \quad (9)$$

$$b = f_1(1 + p_2^{(0)} f_2) + \gamma(1 + p_1^{(0)} f_1 + p_2^{(0)} f_2)(1 + p_1^{(0)} f_1 + p_2^{(0)} f_2 + f_2 \Delta p_2(t)), \text{ (MPa}^{-1}\text{)} \quad (10)$$

$$c = p_1^{(0)} f_1 f_2 (p_2^{(0)} + \Delta p_2(t)). \quad (11)$$

Solution of the quadratic equation (8) respectively to the unknown function $\Delta p_1(t)$ gives a dependence of the excess pressure of gaseous methane on time

$$\Delta p_1(t) = (b/2a) \cdot \left(\sqrt{1 + 4(ac/b^2)} - 1 \right), \text{ (MPa)}. \quad (12)$$

The substitution of the found dependence $\Delta p_1(t)$, (MPa) into the expression (5) allows to determine how the degree of coverage of the adsorption layer by methane molecules $\theta_1(t)$, (dimensionless coefficient) changes depending on the inflow of water vapor into a closed cavity $\Delta p_2(t)$. This dependence is of particular interest in the case of small cavities.

4. Results and discussion

The explicit temporary dependence of the quantity $\Delta p_1(t)$, (MPa) described by the expression (12) should be found to study the evolution of excess pressure of methane in the gaseous phase inside the cavity of the coal substance in the form of cracks and pores, due to the penetration of the water vapor into them. This involves finding the numerical values of the coefficients a , b , c . For this, the numerical values of parameters $\gamma_p, \gamma_{cr}, p_1^{(0)}, p_2^{(0)}, f_1, f_2$, and the time dependence of the water vapor

pressure $\Delta p_2(t)$ (MPa) in the closed cavity should be known. It follows from physical considerations that the pressure of water vapor $p_2(t)$, (MPa) inside a closed cavity changes over some characteristic time τ_f , (s) from a certain minimum initial value $p_2^{(0)}$, (MPa) to a maximum value $p_{2,T}$, (MPa) equal to the pressure of saturated water vapor corresponding to temperature T , (K). For the simplicity, in a coal seam with an extremely low moisture content, it can be assumed that at the initial moment of time there is no partial pressure of water vapor inside the cavity, i.e. $p_2^{(0)} = 0$, or $p_2(t) \equiv \Delta p_2(t)$, (MPa). We extrapolate this function by an expression of the following form:

$$\Delta p_2(t) = p_{2,T} \cdot \text{th} \delta t, \text{ (MPa)}. \quad (13)$$

Here we suppose that $\delta \equiv \tau_f^{-1} = 0.001 \text{ s}^{-1}$ is an inverse characteristic time τ_f , (s) of the penetration of water vapor into closed cracks and pores containing the adsorbed methane on their inner surface. Assuming the temperature $T = 300 \text{ K}$ inside the cavity the pressure of saturated water vapor $p_{2,T} = 3.57 \text{ kPa}$ in this case, according to [9]. A graph of the dependence (13) showing that the state of saturation of water vapor inside the closed cavity is reached is shown in Fig. 1.

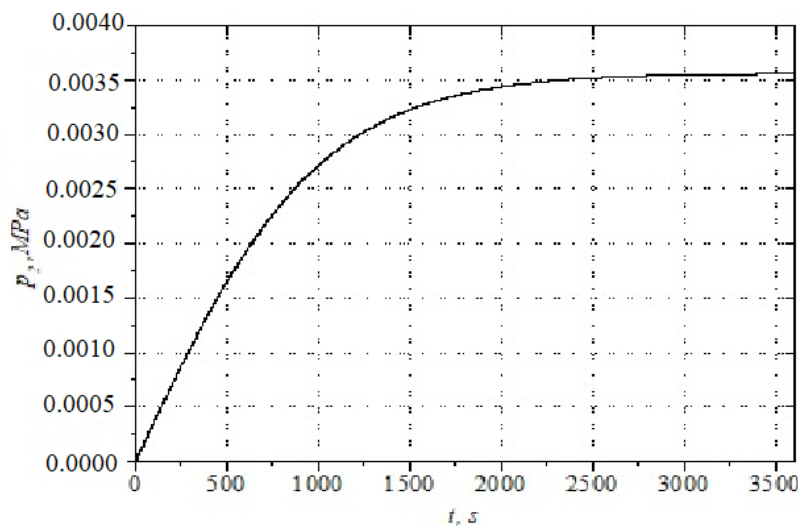


Figure 1 – Time dependence of the partial pressure of water vapor in closed cracks and pores (in MPa) according to the expression (13). The abscissa axis is the time in seconds

Let us consider the simple case of the absence of water vapor inside the cavity at the initial moment of time $p_2^{(0)} = 0$. Then coefficients a , b , c . in the equation (12) become easier and take the form

$$\tilde{a} = \gamma f_1(1 + p_1^{(0)} f_1), \text{ (MPa}^2\text{)}; \quad (14)$$

$$\tilde{b} = f_1 + \gamma(1 + p_1^{(0)} f_1)(1 + p_1^{(0)} f_1 + f_2 \Delta p_2(t)), (MPa^{-1}); \quad (15)$$

$$\tilde{c} = f_1 f_2 p_1^{(0)} \Delta p_2(t). \text{ (dimensionless coefficient)} \quad (16)$$

If the coal seam is gas-saturated, then the pressure of methane $p_1^{(0)}$ inside cracks and pores can be assumed to be equal to 1 MPa.

First of all, characteristic value of the saturated vapor pressure of methane $p_{1,T}$ corresponding to the temperature T should be found. It follows from [10] that for the temperature $T = 300$ K the saturation pressure for methane is $p_{1,T} \approx 30 \text{ MPa} = 3 \cdot 10^7 \text{ Pa}$. Besides, the binding energies of methane and water molecules with a carbon matrix should be found. Experiments show that binding energy of methane molecules with coal is $u_1 = -13.5 \text{ kJ/mol}$ [10, 11] and the binding energy of water molecules with coal substance is $u_2 = -19.0 \text{ kJ/mol}$ [12]. Let the adsorption of water vapor occurs at a temperature $T = 300$ K. Then we have a value $RT \approx 2.5 \text{ kJ/mol}$ for this temperature, where R is a universal gas constant. According to this we find $u_1/RT = 5.4$ and $u_2/RT = 7.6$. Now we can use expressions (2) to calculate parameters f_1 and f_2 that become equal to $f_1 = 7.4 \cdot 10^{-6} \text{ MPa}^{-1}$, $f_2 = 0.56 \text{ MPa}^{-1}$.

At first we consider pores of various spatial scales as a cavity in a coal. To estimate the numerical value of the parameter γ_p , (MPa^{-1}) in the case of a pore, we use the expression $\gamma_p = (\partial p / \partial \mathcal{G})^{-1} = (r \sigma_m / 3 k_B T)$, where k_B (kJ/K) is a Boltzman constant, r , (m) is a radius of a pore. The data obtained for the pores are presented below in Table. 1.

Table 1

r_p, m	10^{-3}	$3 \cdot 10^{-6}$	$2 \cdot 10^{-6}$	10^{-6}
$\gamma_p, \text{MPa}^{-1}$	$1.6 \cdot 10^{-2}$	$4.8 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$

For a cavity in the form of a crack, we have $\gamma_{cr} = (\partial p / \partial \mathcal{G})^{-1} = (z \sigma_m / k_B T)$, where z , (m) is a gaping crack. The data obtained for cracks are presented below in Table. 2.

Table 2

z, m	10^{-3}	$0.3 \cdot 10^{-6}$	$0.2 \cdot 10^{-6}$	$0.1 \cdot 10^{-6}$
$\gamma_{cr}, \text{MPa}^{-1}$	$4.8 \cdot 10^{-2}$	$1.44 \cdot 10^{-5}$	$9.6 \cdot 10^{-6}$	$4.8 \cdot 10^{-6}$

At the same time, it should be accounted that the area per one sorption molecule of methane is equal to $\sigma_m = 0.2 \text{ nm}^2$ [13]. Using the found values of the parameters,

we will find the coefficients $\tilde{a}, \tilde{b}, \tilde{c}$. Substitution of these parameters in expressions (14) – (16), gives the next values of the coefficients mentioned above through the parameter γ :

$$\tilde{a} \approx 6.2 \cdot 10^{-5} \gamma, MPa^{-2}; \quad (17)$$

$$\tilde{b} \approx 7.4 \cdot 10^{-6} + 70.56 \cdot (1 + 238th(0.001t))\gamma, MPa^{-1}; \quad (18)$$

$$\tilde{c} \approx 1.48 \cdot th(0.001t), \text{ (dimensionless coefficient)}. \quad (19)$$

By substituting these values of coefficients into the equation (12), we find the desired dependence of excess pressure inside macropores and macrocracks as a function of time $\Delta p_1(t), (MPa)$.

$$\Delta p_1(t) \approx 0.57(1 + 238th(0.001t)) \times \left(\sqrt{1 + 7.4 \cdot 10^{-4} th(0.001t) / \gamma (1 + 238th(0.001t))^2} - 1 \right). \quad (20)$$

Using dependence (20), it is possible to analyze the time evolution of the excess pressure of methane $\Delta p_1(t), (MPa)$ in the cavities of the coal substance as a result of their saturation with water vapor. The time dependence of the excess pressure in a macropore of radius $10^{-3}m$ is shown in Fig. 2.

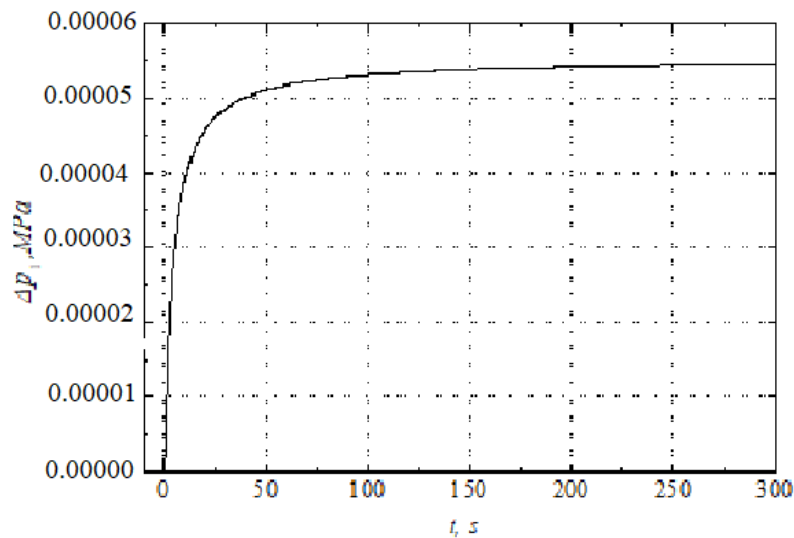


Figure 2 –Evolution of the excess pressure of gaseous methane (in MPa) in macropores of radius $r = 10^{-3}m$ due to its desorption from the inner surface of the pore after coal moistening. The initial pressure of methane is $1 MPa$. The abscissa axis is the time in seconds

As can be seen, due to the desorption of methane from the inner surface of a closed pore, the pressure of gaseous methane in it reaches saturation in just 5 minutes

and increases insignificantly from 1 *MPa* to only 1.000055 *MPa*. Moreover, according to the Fig. 1, this happens long before the partial pressure of water vapor reaches saturation, namely at the pressure of water vapor about $p_2 \approx 1 \text{ kPa}$. So, in the Langmuir approximation (i.e., a single-layer adsorption layer), the excess pressure of gaseous methane in macropores turns out to be negligible due to its desorption from the inner surface. Taking into account the fact that in a real situation the covering of the adsorption layer may become a multilayer, this excess pressure will be several times higher.

Now we consider what is observed when the water vapor enters the micropore, i.e. into micron-sized pores, when the pore radius is of the order of 10^{-6} m . In this case, by substituting expressions (17) – (19) into (12), we obtain

$$\Delta p_1(t) = (0.06/\gamma + 0.57 \cdot (1 + 238th(0.001t))) \times \\ \times \left(\sqrt{1 + \frac{3.67\gamma th(0.001t)}{[7.4 \cdot 10^{-6} + 70.56\gamma(1 + 238th(0.001t))]^2}} - 1 \right), \text{ MPa} \quad (21)$$

The dependence of the excess pressure in micropores as a function of time is shown in Fig. 3.

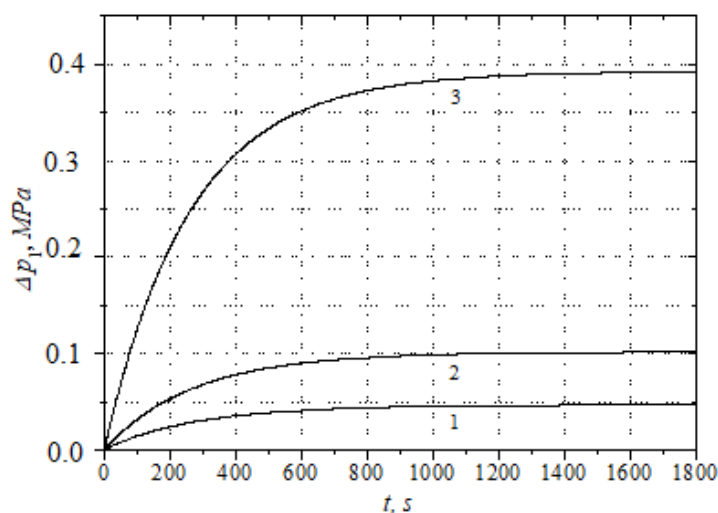


Figure 3 – Evolution of the excess pressure of gaseous methane (in *MPa*) in micropores due to its desorption from the inner surface of the pore. Curves 1–3 correspond to the pore radii $3 \cdot 10^{-6} \text{ m}$; $2 \cdot 10^{-6} \text{ m}$; 10^{-6} m respectively. The initial pressure of methane is 1 *MPa*

As can be seen from this figure, the relative change in the gaseous component inside such micropores is more significant. Expression (21) can describe the evolution of the excess pressure in the case of microcracks, using the corresponding values γ_{cr} from Table. 2.

Analysis of the observed phenomena in micropores shows that the relatively change of the gaseous component of methane $\Delta p_1 / p_1^{(0)}$ (dimensionless coefficient)

inside micropores of the radii $3 \cdot 10^{-6} m$; $2 \cdot 10^{-6} m$; $10^{-6} m$ becomes more perceptible and is 5%; 10%; 39% respectively (Fig. 3).

The time dependence of the excess pressure in cracks is calculated similarly.

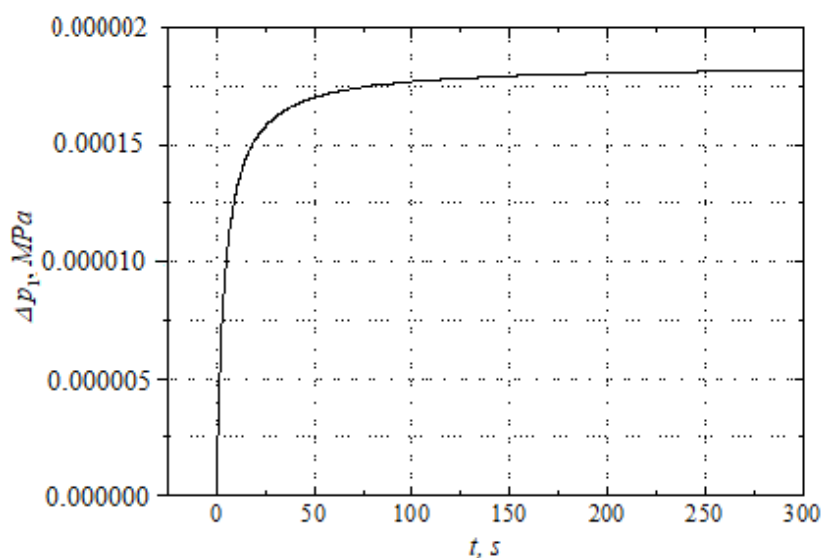


Figure 4 – Evolution of the excess pressure of gaseous methane (in *MPa*) in a macrocrack with a gap of $10^{-3} m$ due to desorption from the inner surface of the crack after coal moistening. The initial pressure of methane is 1 *MPa*

The time evolution of the excess pressure of methane $\Delta p_1(t)$, (*MPa*) in a crack with a gap $10^{-3} m$ after coal moistening upon the initial value of pressure in gaseous methane in 1 *MPa* is presented in Fig. 4.

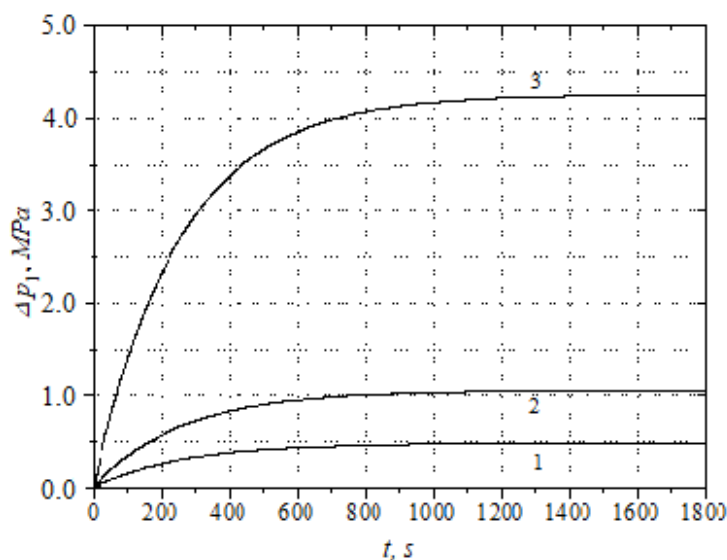


Figure 5 – Evolution of the excess pressure of gaseous methane (in *MPa*) in microcracks with gaps $0.3 \cdot 10^{-6} m$; $0.2 \cdot 10^{-6} m$; $0.1 \cdot 10^{-6} m$ respectively, due to its desorption from the inner surface of cracks. The initial pressure of methane is 1 *MPa*

As can be seen, due to the desorption of methane from the inner surface of a closed crack, the pressure of gaseous methane in it increases insignificantly from

1 MPa to only 1.0000182 MPa. Thus, in the Langmuir approximation (i.e. a single-layer adsorption layer), the excess pressure of gaseous methane in macrocracks due to its desorption from the inner surface turns out to be negligible. Taking into account that in a real situation the coating of the adsorption layer may turn out to be multi-layer, this excess pressure is many times greater.

Then, the increase in an excess pressure of methane in microcracks due to its desorption from the inner surface of the crack was analyzed.

The time dependence of the excess pressure in microcracks is calculated similarly. The numerical values of the parameter γ_{cr} , (MPa⁻¹) for microcracks with gaps $0.3 \cdot 10^{-6} m$; $0.2 \cdot 10^{-6} m$; $0.1 \cdot 10^{-6} m$ are presented in Table 2. The analysis of the observed phenomena in microcracks shows that the relative change in the gaseous component of methane $\Delta p_1 / p_1^{(0)}$ (dimensionless coefficient) inside the microcracks with gaps $0.3 \cdot 10^{-6} m$; $0.2 \cdot 10^{-6} m$; $0.1 \cdot 10^{-6} m$ turns out to be already more noticeable and amounts to 50%; 110% and 430% respectively, (Fig. 5). It will be significant mainly for microcracks with gaps of the order of tenths of microns.

5. Conclusions

Our study shows that moistening of coal causes the methane desorption from the inner surface of gas-filled cracks and pores, which leads to an increase in the pressure of gaseous methane in them. Evolution curves show that the increase of pressure occurs much faster for macropores and macrocracks than for microcracks and micropores. However, for pores and cracks of the macroscopic scale this phenomenon does not lead to the significant change in pressure of the gaseous component inside the cavity. A noticeable effect is manifested only in gas-saturated micron-sized pores or in gas-saturated microcracks with gaps of the order of tenths of a micron. If this phenomenon is not dangerous for pores, then it can be critical for cracks, causing microcracks to increase in size, especially when they are located near macroscopic cavities.

REFERENCES

1. Zhi, S. and Elsworth, D. (2016), "The role of gas desorption on gas outbursts in underground mining of coal", *Geomech. Geophys. Geo-energ. Geo-resour.*, vol. 2, no. 3, pp. 151–171. <http://dx.doi.org/10.1007/s40948-016-0026-2>
2. Zhang, L., Ren, T. and Aziz, N. (2014), "Influences of temperature and moisture on coal sorption characteristics of a bituminous coal from the Sydney Basin, Australia", *International Journal of Oil, Gas and Coal Technology*, vol. 8, no. 1, pp. 62–78. <https://doi.org/10.1504/IJOGCT/2014.064429>
3. Guo, H., Cheng, Y., Wang, L., Lu, S. and Jin, K. (2015), "Experimental study on the effect of moisture on low-rank coal adsorption characteristics", *Journal of Natural Gas Science and Engineering*, vol. 24, pp. 245–251. <https://doi.org/10.1016/j.jngse.2015.03.037>
4. Nie, B., Liu, X., Yuan, S., Ge, B., Jia, W., Wang, C. and Chen, X. (2016), "Sorption characteristics of methane among various rank coals: impact of moisture", *Adsorption*, vol. 22, no. 3, pp. 315–325. <https://doi.org/10.1007/s10450-016-9778-9>
5. Wang, L., Chen, E., Liu, S. and et al., (2017), "Experimental study on the effect of inherent moisture on hard coal adsorption-desorption characteristics", *Adsorption*, vol. 23, no.5, pp. 723–742. <https://doi.org/10.1007/s10450-017-9889-y>
6. Wang, Z., Su, W., Tang, X. and Wu, J. (2018), "Influence of water invasion on methane adsorption behavior", *International Journal of Coal Geology*, vol. 197, pp. 74–83. <https://doi.org/10.1016/j.coal.2018.08.004>
7. Yang, Y., Lin, L., Li, M., Zhang, X., Yang, C., Wang, Y., Fan, B., Chen, C. and Luo, W. (2019). "A Multi-Scale Modeling of CH₄ and H₂O Adsorption on Coal Molecules and the Water Blocking Effect in Coalbed Methane Extraction", *Applied Sciences*, vol. 9, no. 3421, pp. 1–12. <https://doi.org/10.3390/app9163421>
8. Stefanovich, L.I., Feldman, E.P. and Mazur, O.Yu. (2021), "Effect of water vapor on the process of methane desorption from coal", *Physico-tekhnicheskie problemy gornogo proizvodstva*, no. 23, pp. 22–39. <https://doi.org/10.37101/ftpgp23.01.002>

9. Stull, R. (2016), *Practical Meteorology: An Algebra-based Survey of Atmospheric Science*, University of British Columbia, Vancouver, Canada.
10. Friend, D., Ely, J., and Ingham, H. (1989), "Thermophysical Properties of Methane", *J. Phys. Chem. Ref. Data*, <https://doi.org/10.1063/1.555828>
11. Vasilkovskiy, V., Minieiev, S. and Kalugina, N. (2019), "Bonding energy and methane amount at the open surface of metamorphic coal", *Essays of Mining Science and Practice. E3S Web of Conferences*, p. 109. <https://doi.org/10.1051/e3sconf/201910900108>
12. Jenness, G.R., Karalti, O. and Jordan, K.D. (2010), "Benchmark Calculations of Water–Acene Interaction Energies: Extrapolation to the Water–Graphene Limit and Assessment of Dispersion–Corrected Dft Methods", *Phys. Chem. Chem. Phys.*, vol. 12, pp. 6375–6381. <https://doi.org/10.1039/c000988a>
13. Gragg, S. and Sing, K. (1984), *Adsorbtsiya, udel'naya poverkhnost', poristost'* [Adsorption, specific surface area, porosity], Mir, Moscow, USSR.

About the authors

Stefanovych Leonid Illich, Doctor of Physical and Mathematical Sciences (D.Sc.), Senior Researcher in Department of Physics of Coal and Rocks, Deputy Director of the Research Department, Branch for Physics of Mining Processes of the M.S. Poliakov Institute of Geotechnical Mechanics of the NAS of Ukraine, Dnipro, Ukraine, lstef2591@gmail.com.

Feldman Eduard Petrovych, Doctor of Physical and Mathematical Sciences (D.Sc.), Chief Researcher, Department of Physics of Coal and Rocks, Branch for Physics of Mining Processes of the M.S. Poliakov Institute of Geotechnical Mechanics of the NAS of Ukraine, Dnipro, Ukraine, edward.feldman.40@gmail.com

Mazur Olha Yuriivna, Doctor of Philosophy (Ph.D.), Technical University of Liberec, Liberec, Czech Republic, O.Yu.Mazur@gmail.com

ВИТІСНЕННЯ АДСОРБОВАНОГО МЕТАНУ ВОДЯНОЮ ПАРОЮ В ЗАМКНУТІЙ ПОРОЖНИНІ ВУГІЛЬНО-ПОРОДНИХ ПЛАСТІВ

Стефанович Л.І., Фельдман Е.П., Мазур О.Ю.

Анотація. У газонасиченому вугільному масиві закриті тріщини та пори крім вільного метану містять метан, який пов'язаний з адсорбційними центрами на їх внутрішніх поверхнях. Відомо, що внаслідок потрапляння води у вигляді водяної пари всередину цих порожнин адсорбований метан має тенденцію до переходу його з адсорбційного шару до газоподібної фази. Мета цієї роботи – з'ясувати наскільки істотним буде підвищення тиску газоподібного метану в замкнених порожнинах вугільної матриці за рахунок його десорбції з внутрішньої поверхні пор і/або тріщин в результаті потрапляння в них води у вигляді водяної пари. Задача вирішується в припущенні, що підвищення парціального тиску водяної пари всередині тріщин і пор відбувається в результаті фільтраційних явищ, тобто доволі повільно порівняно з адсорбційно-десорбційними процесами, що відбуваються на внутрішніх поверхнях порожнин вугільної речовини.

При розрахунку надлишкового парціального тиску метану, що виник у результаті витіснення його з адсорбційного шару молекулами води, для ступенів покриттів адсорбційного шару молекулами метану і води використано наближення Ленгмюра, тобто наближення одношарової адсорбції. Показано, що у разі порожнеч макроскопічного розміру порядку 10^{-3} м і більше це явище є незначним. Однак для газонаповнених закритих порожнин розміром порядку мікрметрів і менше і з початковим тиском газоподібного метану порядку 1 МПа відносний надлишковий тиск газоподібного метану в результаті його десорбції з внутрішньої поверхні закритих тріщин і пор може становити десятки відсотків.

Наукова новизна роботи полягає в тому, що розрахунки, пов'язані з появою надлишкового тиску метану в закритих тріщинах і порах в результаті його витіснення водяними парами з внутрішньої поверхні закритих порожнин вугільної матриці, наскільки відомо авторам, раніше не проводилися. Підвищення тиску газоподібного метану всередині закритих порожнин може призвести до зростання їх розміру, особливо це відноситься до тріщин, які розташовані поблизу порожнеч макроскопічного розміру.

Ключові слова: газонаповнені тріщини і пори, надлишковий газоподібний метан, десорбція, внутрішня поверхня порожнин, водяна пара.