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REGULARITY OF CHANGE IN THE VOLMER DIFFUSION COEFFICIENT OF METHANE ADSORBED IN THE MICROSORPTION STRUCTURE OF THE ELASTIC ZONE OF THE COAL SEAM BEARING PRESSURE

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Abstract. The Volmer diffusion coefficient of methane adsorbed in the micropores of coal in the elastic zone of the coal seam bearing pressure, which normally is under conditions of significant compressive stress, was calculated with taking into account the energy of the methane sorption connection with coal, the energy of Volmer diffusion activation in the porous space of coal, and the stressed state of the elastic zone with its influence on the change of Volmer porosity. During the calculations, such parameters as the diameter of Volmer micropores and the length of the descending branch of the bearing pressure diagram were varied. As a result of the approximation of these calculations, both pairwise dependences of the Volmer diffusion coefficient on the listed parameters and its multifactorial relationship with them were established. Therefore, it is concluded that the process of methane diffusion in the elastic zone of bearing pressure is not blocked by the rock pressure, as previously thought, but is actively developing. The diffusion of free methane will be determined by the established regularity of changes in the Volmer diffusion coefficient in the elastic zone of the coal seam bearing pressure. The calculations show that as the distance from the maximum of the bearing pressure increases, the Volmer diffusion coefficient of methane in the coal seam increases, which is due to a decrease in the pressure of rocks in the descending branch of the bearing pressure diagram. However, this growth is not great due to the weak compressibility of pores. Therefore, for pores of the same diameter, the Volmer diffusion coefficient in the elastic zone of the coal seam bearing pressure for the given mining geological conditions can be considered a constant. For depths of, for example, 1000 m and pore diameters of 10 Å, the value of the Volmer diffusion coefficient will be approximately $3.77 \cdot 10^{-8}$ m²/s. This confirms that methane gas release is caused not only by filtration of free gas, but also by Volmer diffusion of adsorbed methane. In turn, the reserves of the latter are known to be the main reserves of methane in coal. Therefore, the established regularity makes it possible to more accurately calculate the volumes of methane, which will be released from the coal massif during mining operations, in order to assess safety of conditions for coal deposits mining and to develop technologies for coal mine methane production.

Keywords: adsorbed methane, microstructure of a coal seam, Volmer pores, area of bearing pressure, elastic zone, Volmer diffusion coefficient.

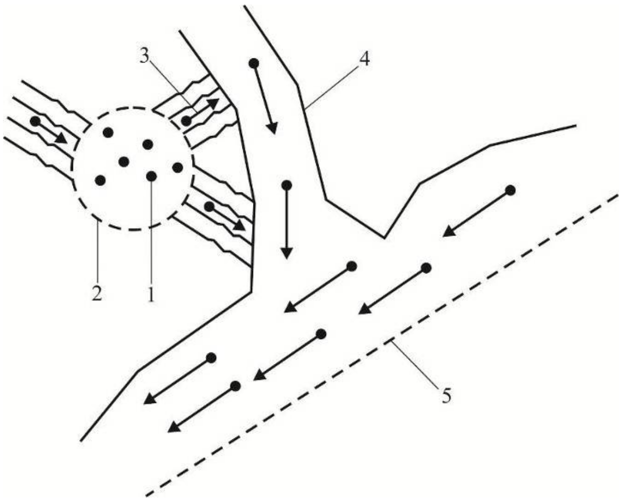
1. Introduction

Today, when developing the highly efficient technologies for coal and CMM production, the main live task is to establish the regularities of diffusion-filtration flows of methane mass transfer in the coal massif. At the same time, one of the most important areas in the carbon-based massif during mining operations is an elastic area of the bearing pressure, which determines the volumes and regularities of methane release into the mined-out space of the mining massif. For many years, it was believed that since this zone was under significant mining pressure, the mass transfer of methane was blocked in it, a priori, due to the compression mechanism of the coal structure deformation. However, the data of recent studies have shown that the mechanism of methane mass transfer in the elastic zone of the bearing pressure is more complicated due to the diversity of the hierarchical structure of coal [1, 2], which causes different types of diffusion in the coal seam, in particular, Volmer diffusion [3]. The latter is important because it connects solid-state diffusion [4] with the diffusion of free methane. Besides, it overcomes the forces of interphase interaction between methane and coal, which are important factor for gas-dynamic phenomena development in the mining massif. Therefore, the purpose of this work was to investigate the change in the Volmer diffusion coefficient of methane desorbed from the microsorption structure of the elastic zone of the coal seam - from the maximum bearing pressure to the virgin massif during mining operations.

The purpose of the work - to establish the regularity of changes in the Volmer diffusion coefficient of methane in the microsorption structure of the elastic zone of the coal seam bearing pressure.

2. Methods

It is known that the hierarchical microstructure of the coal medium, which forms various desorption channels in itself, can be represented by the scheme shown in Figure 1. With taking into account this scheme, the process of methane desorption during the gas release from the coal medium will proceed in the following way. Since the main volumes of adsorbed methane are located in the micropores of coal, its gas release will be directed to the area of the lowest sorption pressure. That is, in the initial period, desorption is directed to supermicropores and mesopores (Fig. 1) according to the law of solid-state diffusion. Further, this process will develop towards the interlayer space according to the law of Vollmer diffusion. Free diffusion will take place in the interlayer space, and free methane filtration will take place in the macrocracks (Fig. 1).



1 – methane molecule; 2 – micropore wall; 3 – supermicropores and mesopores, where Volmer diffusion takes place; 4 – interlayer space; 5 – macrocrack

Figure 1 – The scheme of desorption channels during methane gas release from the hierarchical structure of the coal medium

Beyond the zone of maximum bearing pressure, the Volmer pores will be compressed. The dimensions of these pores depend on the stress state in this zone. The diameter of the Volmer pores can be determined from the ratio [5]:

$$d_f = d_{f0}\sqrt{\frac{\varepsilon_i}{\varepsilon'_{\gamma H}}}, \qquad (1)$$

where d_{f0} is the diameter of the Volmer pore in the undisturbed coal massif; ε_i, $\varepsilon'_{\gamma H}$ is the porosity of coal in the unloaded and loaded massif, respectively, at a depth H in rocks with specific gravity – γ (N/m^2). The latter are described by exponential functions presented in [6].

As the calculations by formula (1) show, diameters of the Volmer pores in the zone of the bearing pressure vary within (12–8) m. At the same time, according to [1], the main parameters, which describe the state of methane adsorbed in these pores, are the energy of adsorption – Q, the energy of Volmer diffusion activation – E_{af}, and the reservoir temperature – T. For the smallest Volmer pores, these parameters are equal to Q = 9100 J/mol, E_{av} = 6500 J/mol [7]. For larger pores, these parameters can be approximated by exponential functions in the form of [7]:

$$Q(df) = D_Q + A_Q \exp(-d_f / t_Q); \tag{2}$$

$$E_{af}(d_f) = D_E + A_E \exp(-d_f / t_E), \tag{3}$$

where the first component in (2)–(3) sets the value of the parameter when the pore diameter tends to infinity; A_i is amplitude of the parameter change; t_i is the rate of the parameter change when the pore diameter changes.

In general, the Volmer diffusion coefficient can be determined by the formula [8]:

$$D_f = D_{0f} \cdot \sqrt{T} \exp\left(\frac{Q - E_{af}}{R_г T} \right), \tag{4}$$

where D_f is the Volmer diffusion coefficient, m^2/s; D_{0f} is pre-exponential factor, m^2/(s·K); Q is adsorption energy, J/mol; $R_г$ is gas constant, J/(mol·K); E_{av} is the energy of Volmer diffusion activation, J/mol; T is temperature, K.

The average temperature, for example, at depths of the order of 1000 m will be T=307.9 K [9].

The pre-exponential factor D_{0f} in formula (4) will also depend on the diameter of the pores. Its numerical values are presented in Table 1.

Table 1 – Numerical values of the D_{0f} parameter for some pores [7].

$D_{0f}\times10^{11}$, m^2/(s·K)	Diameters of pores, m		
	8	10	12
	3.21	4.44	5.75

Therefore, the ratio (4) with taking into account the approximate dependencies (2)–(3) and the data in Table 1 allows establishing the Volmer diffusion coefficient of methane in the zone of maximum bearing pressure for different pore diameters. The range of changes in the diameters of the Volmer pores in the elastic zone of the bearing pressure at different distances from its maximum can be established by formula (1).

3. Results and discussion

The results of the calculation of the change in the Volmer diffusion coefficient of methane in the coal pore with initial diameter of 12 m in the elastic area of the bearing pressure are presented in Fig. 2

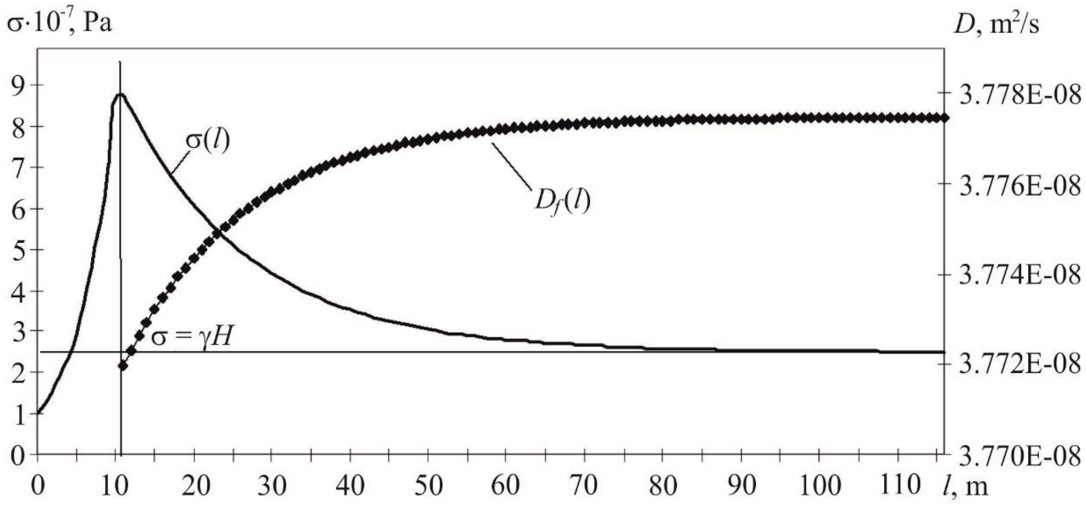


Figure 2 – The regularity of changes in the Volmer diffusion coefficient of methane D_v in the coal pore with diameter of 12 m in the elastic zone of the bearing pressure σ(*l*)

As data in Fig. 2 show, the Volmer diffusion coefficient of methane changes slightly with increase of distance from the maximum bearing pressure – *b*. However, in this case, there is a large length of the stabilization section. Therefore, expression (4) was approximated by an exponential function similar to formulas (2) and (3) in the form of:

$$D_v = D_{0f} + A_D \, exp(-b / t_D). \qquad (5)$$

The dependence of the Volmer diffusion coefficient of methane on the distance of the maximum of the bearing pressure deep into the massif, i.e., the length of the descending branch of the bearing pressure, for different diameters of the Volmer pores is shown in Fig. 3.

The results of approximating the graphs in Fig. 3 by function (5) are presented in Table 2.

Table 2 – Results of approximation of the dependence of the Volmer diffusion coefficient on the distance parameter of the maximum bearing pressure deep into the massif – *b*.

Diameter of a pore, m	- Approximation parameters		
	D_{0f}, m²/s	- A_D, m²/s	t_D, m
12	$3.77\cdot10^{-8}$	$-8.65\cdot10^{-11}$	15.99238
10	$2.31\cdot10^{-8}$	$-1.09\cdot10^{-10}$	15.9937
8	$6.11\cdot10^{-9}$	$-1.51\cdot10^{-10}$	16.021

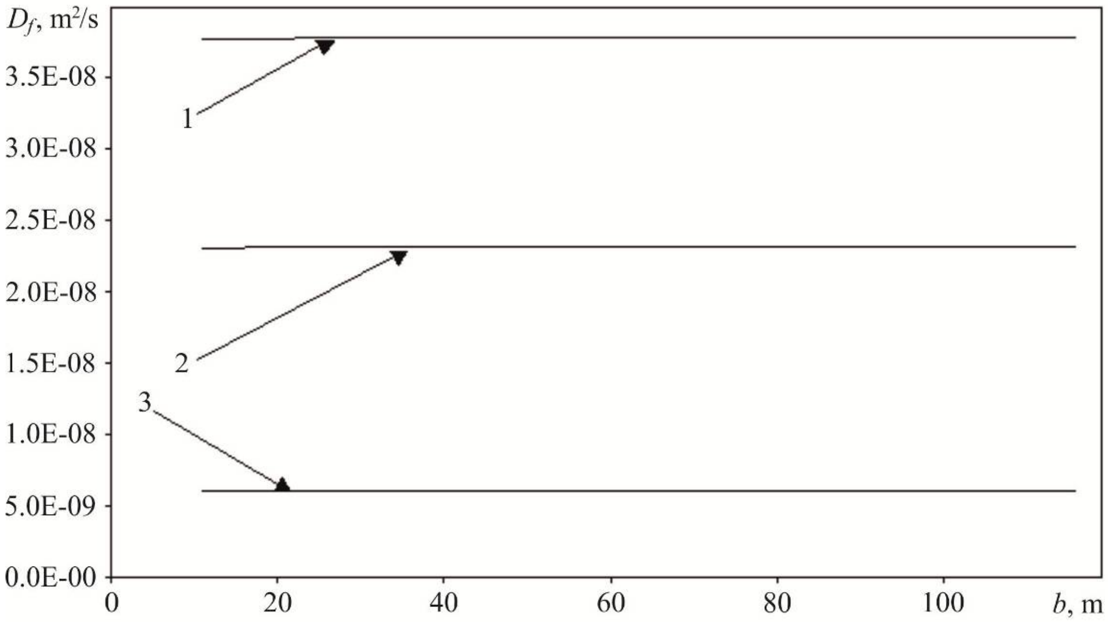


Figure 3 – Dependence of the Volmer diffusion coefficient on the length of the descending branch of the bearing pressure for different pore diameters: 1 – 12 m; 2 – 10 m; 3 – 8 m.

According to the algorithm described above, the data in Table 2 were approximated in order to obtain the dependence of the Volmer diffusion coefficient on the diameter of the Volmer micropores. This was done by using an exponential function in the form (5), where the approximation parameters were replaced for convenience by functions that had the form:

$$D_{0f} = D_1 + A_1\, exp(-d_f / t_1); \tag{6}$$

$$A_d = D_2 + A_2\, exp(-d_f / t_2); \tag{7}$$

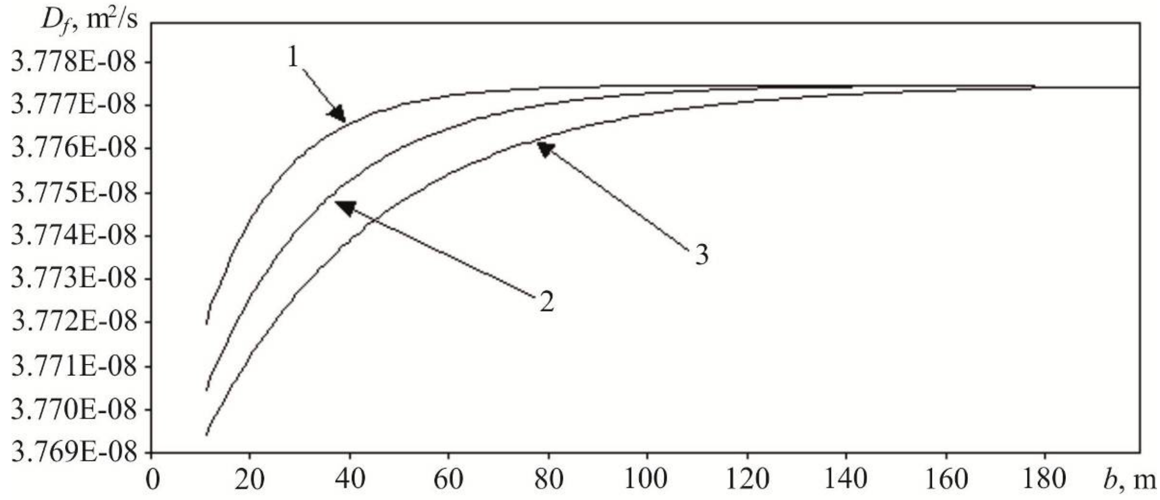
$$t_d = D_3 + A_3\, exp(-d_f / t_3). \tag{8}$$

The results of approximating the data in Table 2 by functions (6) – (8) are presented in Table 3.

Table 3 – Results of approximation of the dependence of the Volmer diffusion of methane in coal on the diameter of micropores

Approximation parameter	- Values
D_1	$1.2679\cdot10^{-7}$
D_2	$-6.08444\cdot10^{-11}$
D_3	15.99231
A_1	$-2.2182\cdot10^{-7}$
A_2	$-1.12714\cdot10^{-9}$
A_3	5.2485702
t_1	13.14218
t_2	3.17427
t_3	0.66023

After that, the dependence of the Volmer diffusion coefficient of methane in coal on the length of the descending branch of the bearing pressure was studied according to the calculation algorithm. The results of calculations of the Volmer diffusion coefficient of methane in coal at different lengths of the descending branch of the bearing pressure for pores with diameter of 12 m are presented in Fig. 4.



1 – *b*=100 m; 2 – *b*=150 m; 3 – *b*=200 m

Figure 4 – Changes in the Volmer diffusion coefficient of methane in coal at different lengths of the descending branch of the bearing pressure – *b*

In order to describe the obtained regularities by dependence on the length of the descending branch of the bearing pressure diagram, the approximation of the obtained data, which changed with the length of the descending branch of the bearing pressure, was performed similar to expressions (6) – (8). As the results of the approximation show, such parameters as D_1, A_1 and t_1 in (6) – (8) do not depend on the length of the descending branch of the bearing pressure diagram, which determine the limit value that the Volmer diffusion coefficient of methane tends to at a distance tending to infinity.

In order to obtain the final dependence of the Volmer diffusion coefficient of methane in coal on micropore diameters and the distance from the maximum bearing pressure deep into the massif, the approximating functions were set as follows:

$$D_i = D_{1i} + A_{1i}\, exp(-b / t_{1i}); \tag{9}$$

$$A_i = D_{2i} + A_{2i}\, exp(-b / t_{2i}); \tag{10}$$

$$t_i = D_{3i} + A_{3i}\, exp(-b / t_{3i}). \tag{11}$$

The results of approximation of functions (9)–(11) are presented in Table 4.

Table 4 – Generalized approximation parameters for determining the Volmer diffusion coefficient of methane

Approximation parameter	Index *i*	
	2	3
D_{1i}	$-6.1124\cdot10^{-11}$	-24.72178
D_{2i}	$-1.15121\cdot10^{-9}$	83.26867
D_{3i}	3.15165	-0.90912
A_{1i}	$9.6757\cdot10^{-14}$	27.32296
A_{2i}	$1.21563\cdot10^{-11}$	12.23113
A_{3i}	0.00909	0.82605
t_{1i}	-94.17467	-250.72274
t_{2i}	-146.3866	108.32334
t_{3i}	-109.76187	-155.82118

By substituting the data of Table 4 into formulas (9)–(11), the values of the approximating parameters in expressions (6)–(8) were specified:

$$D_1 = 1.27\cdot 10^{-07}; \tag{12}$$

$$D_2 = -6.11\cdot 10^{-11} + 9.68\cdot 10^{-14}\exp(-b/-94.17); \tag{13}$$

$$D_3 = -24.72 + 27.32\exp(-b/-250.72); \tag{14}$$

$$A_1 = -2.22\cdot 10^{-07}; \tag{15}$$

$$A_2 = -1.15\cdot 10^{-9} + 1.22\cdot 10^{-11}\exp(b/146.39); \tag{16}$$

$$A_3 = 83.27 + 12.23\exp(-b/108.32); \tag{17}$$

$$t_1 = 13.14218 \tag{18}$$

$$t_2 = 3.15 + 0.009\exp(b/109.76); \tag{19}$$

$$t_3 = -0.91 + 0.83\exp(b/155.82). \tag{20}$$

By substituting formulas (12)–(20) into (6)–(8), the following expressions were established for the parameters of formula (4) in the form of approximation dependence (5):

$$D_{0f} = 1.27\cdot 10^{-07} - 2.22\cdot 10^{-07}\exp(-d_f/13.14218) \tag{21}$$

$$\begin{gathered}A_d = -6.11 \cdot 10^{-11} + 9.68 \cdot 10^{-14} \exp(-b/-94.17) + \\ + (-1.15 \cdot 10^{-9} + 1.22 \cdot 10^{-11} \exp(b/146.39)) \times \\ \times \exp(-d_f/(3.15 + 0.009 \exp(b/109.76)));\end{gathered} \tag{22}$$

$$\begin{gathered}t_d = -24.72 + 27.32 \exp(-b/-250.72) + \\ + (83.27 + 12.23 \exp(-b/108.32)) \times \\ \times \exp(-d_f/(-0.91 + 0.83 \exp(b/155.82))).\end{gathered} \tag{23}$$

In turn, by substituting approximate dependencies (21)–(23) in (5), the regularity of changes in the Volmer diffusion coefficient of methane in the elastic zone of the coal seam bearing pressure is established with taking into account the diameter of the Volmer micropores – d_v and the length of the descending branch of the bearing pressure diagram – b.

Formerly, it was believed that in the elastic zone of the bearing pressure of the coal seam, the diffusion of methane adsorbed from the coal microstructure was blocked by the compressive forces of the rock pressure. However, calculations of the Volmer diffusion coefficient of methane have shown that in this zone, where pore compression occurs, Volmer diffusion, like solid-state diffusion [1, 2, 10], continues to develop. That is, in the elastic area of the bearing pressure, the diffusion process of methane adsorbed in the microstructure of coal is not blocked, but develops fully - from the activation of solid-state diffusion to the development of Volmer diffusion, which leads to the free diffusion of methane in coal. Thus, mass transfer of methane from the undisturbed rock massif to the area of maximum bearing pressure takes place in the elastic zone. Moreover, since it is known that adsorbed methane is connected with the microstructure of coal by the forces of interphase interaction, it will be released in a pulsed way at reaching the desorption activation energy. This can lead to the development of gas-dynamic and fire-hazardous phenomena. Therefore, it is necessary to estimate the outburst hazard of the coal-bearing massif not only by bearing pressure zone in the face area [5], but also by assessment of diffusion processes in the elastic zone. In this regard, the development of methods for forecasting the gas-dynamic hazard of the entire bearing pressure zone of the coal seam is the question of the day. When developing these methods, it is necessary to take into account the results of this work, which are given below in conclusions.

4. Conclusions

1. The regularity of changes in the Volmer diffusion coefficient of methane adsorbed in the microstructure of the elastic zone of the coal seam bearing pressure is determined for different diameters of the Volmer micropores and lengths of the descending branch of the bearing pressure diagram, which is described by relations (5), (21)–(23), which take into account the energy of sorption connection of methane with coal and energy of Volmer diffusion activation.

2. It is established that as the distance from the maximum bearing pressure increases, the Volmer diffusion coefficient of methane in the coal seam increases, which is caused by a decrease in rock pressure in the descending branch of the bearing pressure diagram. This growth is not great due to the weak compressibility of pores. For example, at a depth of 1,000 m, the Volmer diffusion coefficient is $3.775 \cdot 10^{-8}$ m^2/s in the case when the length of the descending branch of the bearing pressure diagram is 200 m, and is $3.772 \cdot 10^{-8}$ m^2/s when the length of the descending branch is 100 m.

3. The performed calculations show that for the same depth of coal deposit development and pores of the same diameter, the Volmer diffusion coefficient in the elastic zone of the coal seam bearing pressure can be considered a constant. Its value is determined from the regularity established in the work.

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ЗАКОНОМІРНІСТЬ ЗМІНИ КОЕФІЦІЄНТА ФОЛЬМЕРІВСЬКОЇ ДИФУЗІЇ МЕТАНУ, АДСОРБОВАНОГО У МІКРОСОРБЦІЙНІЙ СТРУКТУРІ ПРУЖНОЇ ЗОНИ ОПОРНОГО ТИСКУ ВУГІЛЬНОГО ПЛАСТА

Мінєєв С.П., Прусова А.А., Янжула О.С., Мінєєв О.С.

Анотація. Виконані розрахунки коефіцієнта фольмерівської дифузії адсорбованого у мікропорах вугілля метану в пружній зоні опорного тиску вугільного пласта, котра знаходиться в умовах значних компресійних напружень. При цьому враховувалася енергія сорбційного зв'язку метану з вугіллям, енергія активації фольмерівської дифузії у пористому просторі вугілля, а також напружений стан пружної зони та його вплив на зміну фольмерівської пористості. При розрахунках варіювалися такі параметри, як діаметр фольмерівських мікропор і протяжність спадної вітки епюри опорного тиску. В результаті апроксимації цих розрахунків встановлені, як парні залежності коефіцієнта фольмерівської дифузії від перелічених параметрів, так і його багатофакторний зв'язок з ними. Зроблено висновок, що дифузійний процес метану в пружній зоні опорного тиску не заблокований гірським тиском, як рахувалось раніше, а активно розвивається. При цьому дифузія вільного метану буде обумовлена встановленою закономірністю змінення коефіцієнта фольмерівської дифузії у пружній зоні опорного тиску вугільного пласта. Розрахунки показали, що в міру віддалення від максимуму опорного тиску коефіцієнт фольмерівської дифузії метану у вугільному пласті зростає, що обумовлено зниженням тиску гірських порід у спадній вітці епюри опорного тиску. Однак, це зростання не є сильним внаслідок слабкої стисливості пор. Тому для пор одного діаметра коефіцієнт фольмерівської дифузії в пружній зоні опорного тиску вугільного пласта для даних горногеологічних умов можна вважати за константу. Для глибин, наприклад, 1000 м і діаметрів пор 10 м значення коефіцієнта фольмерівської дифузії буде дорівнювати, приблизно, $3.77 \cdot 10^{-8}$ м^2/с. Це підтверджує те, що газовіддачу метану обумовлює не тільки фільтрація вільного газу, але і фольмерівська дифузія адсорбованого метану. В свою чергу, запаси останнього, як відомо, є основними запасами метану у вугіллі. Тому встановлена закономірність дозволяє точніше обчислювати об'єми метану, що буде виділятися з вугільного масиву при гірничодобувних роботах для оцінки безпечних умов відпрацювання вугільних родовищ та при розробці технологій видобутку шатного метану.

Ключові слова: адсорбований метан, мікроструктура вугільного пласта, фольмерівські пори, область опорного тиску, пружна зона, коефіцієнт фольмерівської дифузії.