DOI 10.52209/1609-1825_2022_4_208 UDC 622.411.33:622.817.47

Methane Diffusion in a Nanometer-thick Coal Surface Layer

[1]***MULLAGALIYEVA Liliya,** *Master, Assistant, m_liliya88@mail.ru,*
[1]**BAIMUKHAMETOV Sergazy,** *Dr. of Tech. Sci., Professor, s.baimukhamet@gmail.com,*
[1]**PORTNOV Vassili,** *Dr. of Tech. Sci., Professor, vs_portnov@mail.ru,*
[1]**YUROV Viktor,** *Cand. of Phys. and Math. Sci., Director of SRC, exciton@list.ru,*
[1]*NPJSC «Abylkas Saginov Karaganda Technical University», Kazakhstan, Karaganda, N. Nazarbayev Avenue, 56,*
**corresponding author.*

Abstract. *From the proposed model of the thickness of the surface layer of the coal seam in the Sherubaynura section of the Karaganda basin, it follows that this thickness does not exceed 150 nm. For nanostructures of such sizes, there are size dependences of all the physical properties, including the diffusion coefficient of methane through microcracks in the coal seam. This means that for the methane diffusion in the Fick's equation, one must assume that the diffusion coefficient will also depend on the seam size. The solution of this problem shows that the diffusion of nanometer-thick coal-seam methane significantly differs from that of a massive sample. It is also significant that the methane diffusion in the coal seam depends both on the grade of coal through the diffusion coefficient of a massive sample and on the size factor. In the classical case, there is no such dependence. This affects the mechanism of the methane diffusion through coal, taking into account the structural features of their surface properties during metamorphism of coal seams, especially with changing their depth.*

Keywords: *nanostructure, surface layer thickness, coal, molar mass, mine, basin, seam, structure, atomic layer, carbon, size effect, diffusion, methane, model.*

Introduction

Today, occupational safety in coal mines receives the most attention because of the increasing depth of mining and because of the high methane content of coal seams [1]. However, the passions regarding the origin of coal, as well as methane, have not ceased to this day [2]. This is due to the fact that the processes of carbonification and methane formation in coal took place hundred million years ago. In addition, the nanostructure of coal has just begun to develop, although we are already talking about its impact on sudden emissions of coal and methane [3].

In this work we will talk about the nanostructure of coal seams in the Sherubaynura section of the Karaganda basin and consider how this structure is affected by the process of methane diffusion.

The nature of coal and coal mine methane

The modern theory of the molecular structure of the organic mass of coal with the use of quantum chemistry, thermodynamics and physical kinetics is presented in the work [3]. Today, coal is represented as a polymer, which has stability and consists of some skeleton (core), which is surrounded by a set of lateral aromatic links, which are connected with the core by Van der Waals force [3].

Recently there was work [2], where the authors tested the hypothesis of methane formation from coal, using the methods of biogeochemistry and isotopic methods. In doing so, they relied on the fact that methane in the coal seam is formed by methoxyl groups, which were originally part of the plants from which coal matter is formed. It is shown in the work [4], that methane is produced by microorganisms from more than 30 types of methoxylated aromatic compounds contained in coals. These microorganisms decompose primarily high-molecular-weight organic substances and produce hydrogen, acetic acid, methanol, etc., and then, using these substances, produce methane (Figure 1).

Studies of works [2, 4] show that demethylation occurs during the conversion of lignite to brown coal stage. Since the process itself is biogenic in nature, ^{12}C is extracted from the system and the coal seam is enriched in ^{13}C isotope. It certainly follows from this that the stage of anaerobic decomposition of brown coals and the formation of methane is accompanied by a reduction of the light isotope and its transformation into the isotope ^{13}C (Figure 2). This explains the isotope shift during microbial formation of methane.

Coal seams in the Sherubaynura section

The coal seams in the aforementioned area are well described in work [5]. The characteristic of the Sherubaynura syncline differs from all similar

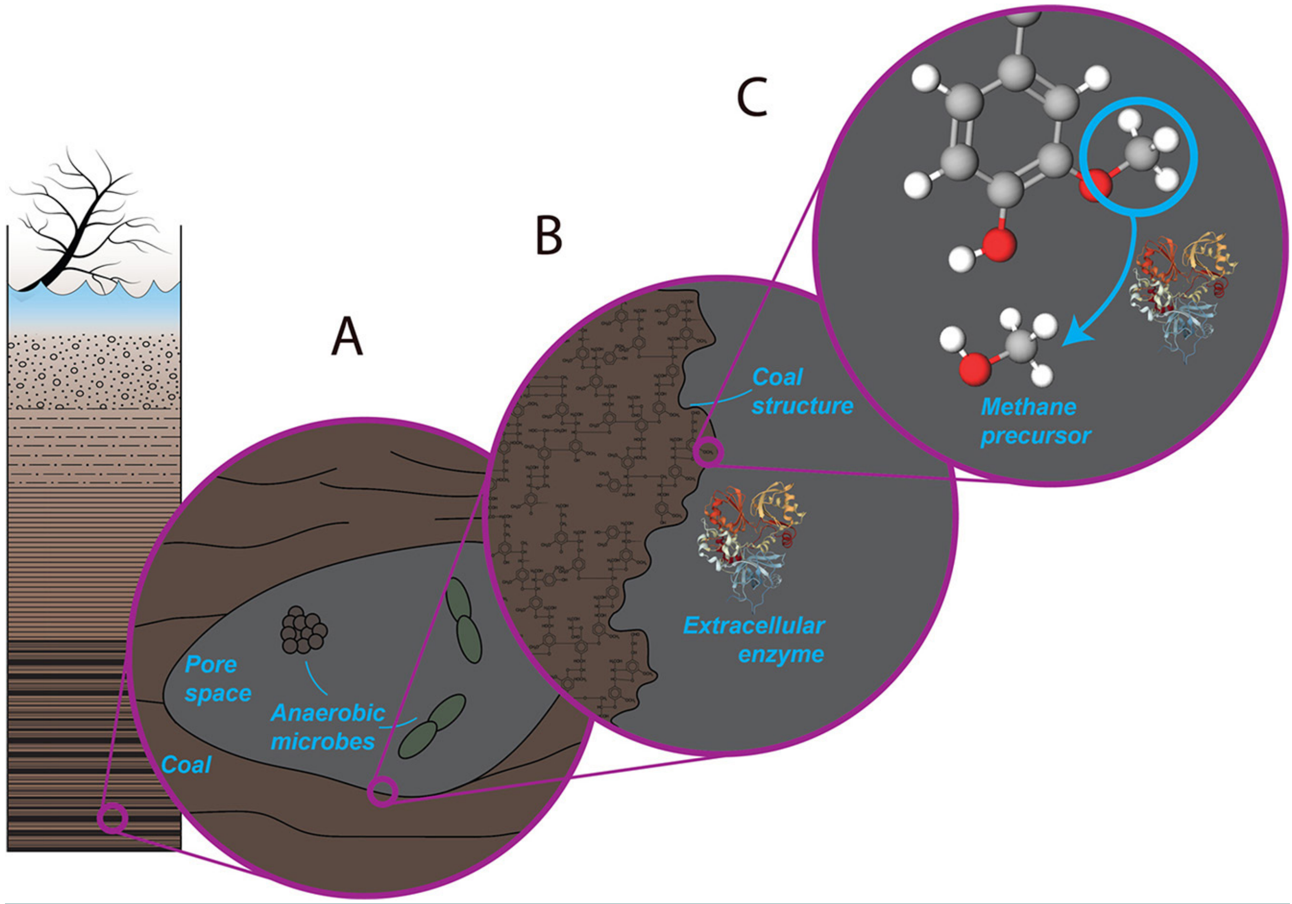


Figure 1 – General diagram of coal seam methane formation with participation of microorganisms: A – anaerobic microbes in the pores of the coal; B – isolation of extracellular enzymes by microorganisms that catalyze the process of demethylation; C – separation of methoxyl groups (methane precursors) from carbon rings [4]

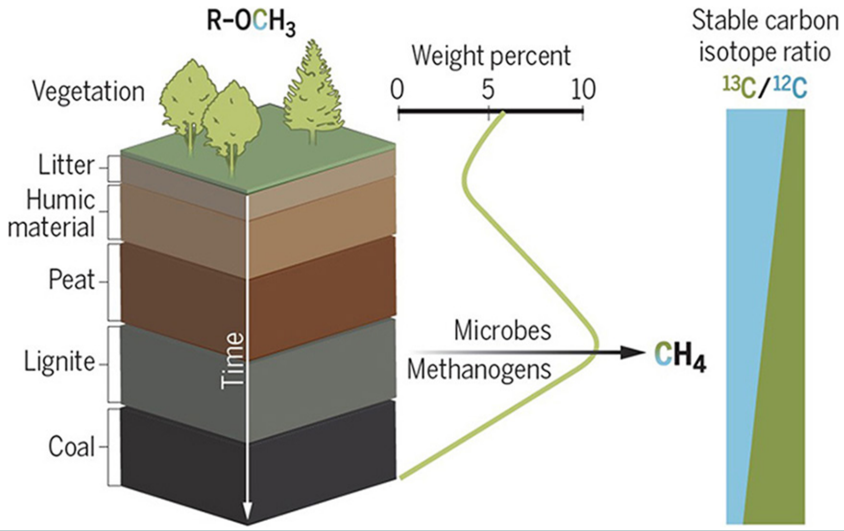


Figure 2 – General diagram of coal seam methane formation [2]

formations in more complex tectonic conditions.

In terms of geology, the Sherubaynura area corresponds to the Palaeozoic and Cenozoic deposits. In the Palaeozoic, hard coal is represented by the following formations: Karaganda, Above-Karaganda, and Ashlyarik. The coal grades are K and OC. Methane of the coal zone is located at the depth of 50 to 150 m. Then, with the depth methane concentration increases and at the depth of 200-250 m it is equal to 10-18 m^3/t g.m.

Its further increase is slower and does not exceed 5-7 m^3 for every 100 m. After reaching a depth of 1000 m, the methane content becomes 22-29 m^3/t g.m. The Langmuir sorption capacity varies from 29.09 m^3/t for sample No. 14 to 31.25 m^3/t for sample No. 3.

As an example, the average value for the three samples is 30.05 m^3/t. The Langmuir pressure varies from 1.08 (sample No. 14) to 1.41 MPa (sample No. 10). The average value for the three samples is 1.27 MPa. Langmuir isotherm curves obtained for coal samples are shown in Figure 4.

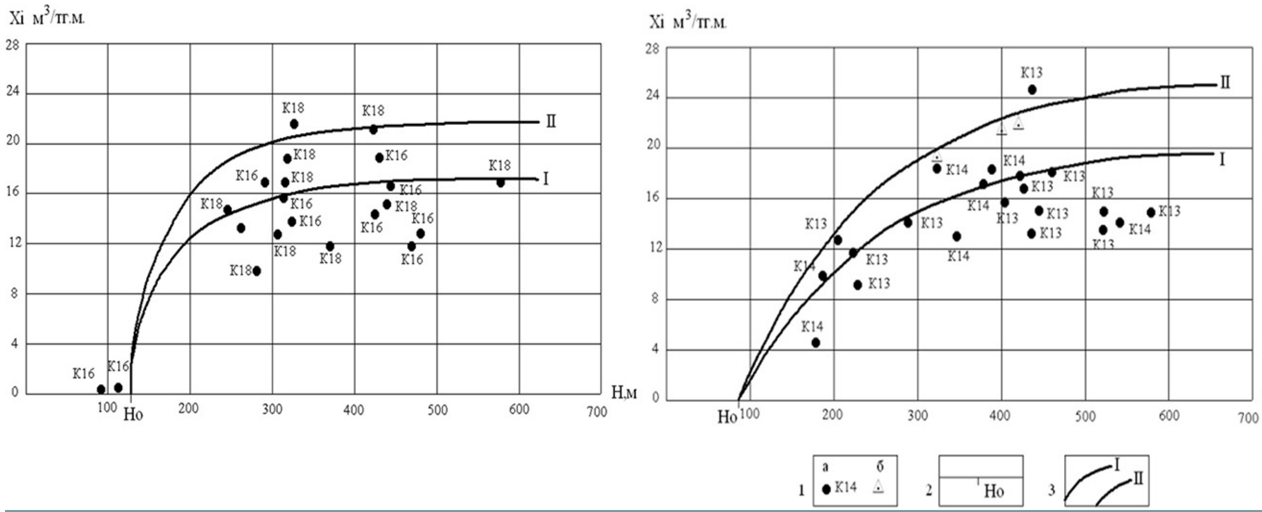
As a result, it is determined that the Langmuir amount of methane is lower than the value of the maximum capacity. Hence, the conclusion follows that the coal seam is in an unsaturated state.

Description of the empirical model

Let's use the results of our articles [6-8]. The thickness of the surface layer in these works is defined as follows:

$$R(I)_M = 0.17 \cdot 10^{-9} v \ (\text{м}). \quad (1)$$

From equation (1) it follows that the thickness of the surface layer depends on one fundamental parameter, which is called the molar (atomic) volume of a chemical element and is equal to $v = M/\rho$, M is the mole mass (g/mol), ρ is the element density (g/cm³).



1 – methane-bearing capacity: a – according to CGS (core gas samplers), b – by methane surveying, 2 – gas recovery zone thickness; 3 – graphs of changes in methane content: I – samples taken without losses, II – samples taken with losses

Figure 3 – Methane content and its changes with depth [5]

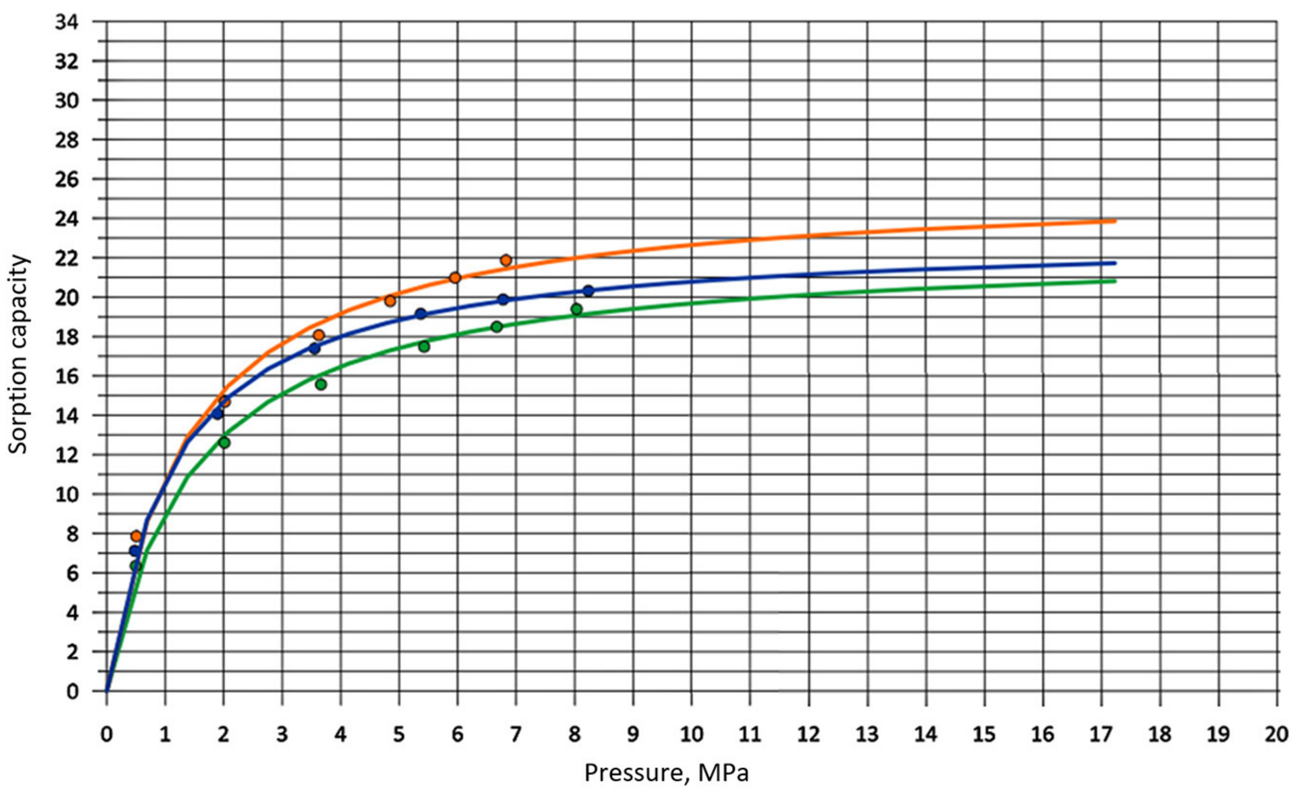


Figure 4 – Langmuir curve [5]

From equation (1) it follows that the thickness of the coal surface layer is determined by the molar mass and its density. We will take the molar mass from work [9], in which the molar mass of the carbon substance is given by the expression:

$$M_{100} = 130.385 \cdot C - 1.941 \cdot O - \\ -14042 \cdot f_e + 461.909 \cdot N, \quad (2)$$

where M_{100} is the atomic mass of carbon in the amount of 100, C, O is the amount of carbon and oxygen, f_e is the aromaticity degree, N is the number of paramagnetic compounds.

Using formulas (1) and (2), let's determine the thickness of the surface layer of coal seams in the Sherubaynura section of the Karaganda basin.

The thickness of the surface layer (Table) $R(I)$ of coal matter, is a nanostructure, but two orders of magnitude greater than the thicknesses of pure metals [6]. Here in parentheses is the number of coal monolayers (~400-500) obtained by dividing $R(I)$ by the average distance (~0.36 nm) between coal macromolecules determined by X-ray scattering (see above). The thickness of the surface layer $R(I)$ of the carbon substance exceeds the technological limit equal to 100 nm according to Gleiter [10]. A peculiarity of the surface layer $R(I)$ is that dimensional effects occur here (Figure 5) [11].

Figure 5, a, b, c is completely similar to Figures 3 and 4. A feature of the $R(I)$ layer are dimensional effects, for which all the atoms are responsible. In other words, we observe collective processes that occur exclusively in nanostructures, they are also called type II dimensional effects [12].

In this layer there are physical and chemical properties of nanomaterials: changing the crystalline (supramolecular) structure of coal; changing its electronic structure and its electrical conductivity; changing the conditions of the stress state of coal; changing the conditions of methane diffusion in coal seams and many other phenomena. In works [6-8] the formula for the description of dimensional effects in any substance, including coal, is proposed:

$$A(h) = A_0 \cdot [1 - R(I)/h],\ h >> R(I), \\ A(h) = A_0 \cdot [1 - R(I)/R(I) + h],\ R(0) < h < R(I), \quad (3)$$

where $A(h)$ is a physical property at the distance h (at depth), A_0 is a physical property in the bulk phase, where there are no dimensional effects.

Methane diffusion in coal seams

Since the works of Krichevsky R.M. (1946), hundred thousand articles have been dealing with the mathematical description of methane transfer from coal seams (for example, [13, 14]). Here we will show how the dimensional effects in the coal matter affect the stationary diffusion of methane, which, in the simplest case, is described by the Fick's law:

$$\frac{d}{dx} = \left(D(x) \cdot \frac{dC(x)}{dx}\right) = 0. \quad (4)$$

If the diffusion coefficient is a constant, i.e., $D(x)=\text{const}$, then we have a simple classical Fick's law. But in the case of the dimensional effect the diffusion coefficient is expressed as follows: $D(x)=D_0[1-R(I)/R(I)+x]$ and equation (4) is transformed to the form:

$$\frac{x}{x+R(I)} \cdot \frac{dC(x)}{dx} = \frac{\delta_1}{D_0}. \quad (5)$$

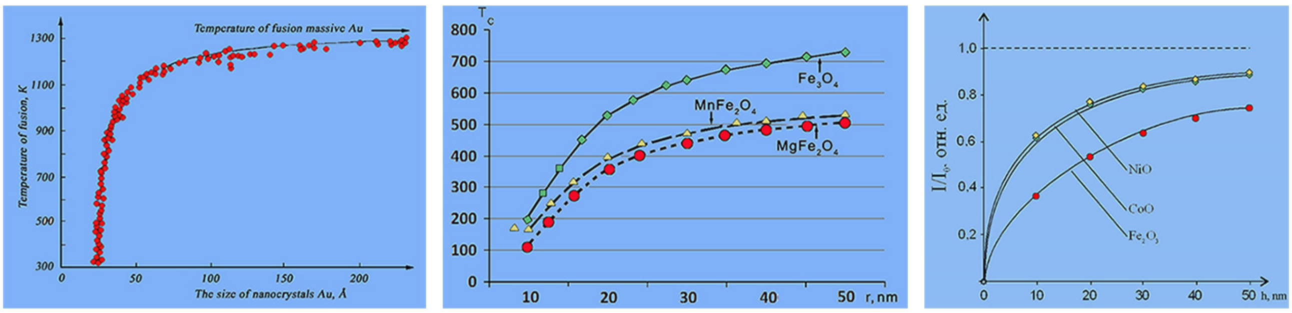
The constant δ_1 represents the integration constant. As a result, equation (5) takes the solution:

$$C(x) = \frac{\delta_1}{D_0}(x + R(I)\ln x) + \delta_2. \quad (6)$$

In the case when the diffusion coefficient in equation (6) is constant, in other words, when $D(x)$ is constant in magnitude, we have the classical Fick

Surface layer thickness of medium coal seams

Coal seam	Coal grade	M – mole mass (g/mol)	ρ – coal density (g/cm^3)	R(I), nm
Sherubaynura section	K	1351	1.27	180.8 (502)
	OC	1340	1.56	146.0 (406)



a b c

Figure 5 – Dimensional dependence of the Au (a), temperature Curie TC (b), luminescence of oxides (c) [6-8]

problem:

$$C(x) = \delta_1 x + \delta_2. \tag{7}$$

However, in equation (6) there is the following feature, namely, in this equation appears the logarithmic term. This unambiguously leads to the fact that the series diverges at the origin of coordinates. Therefore, it is necessary to take the borderline conditions not at the point $x=0$ but on the contrary, at the point $x=0.36$ nm, which is equal to the distance between the crystallographic planes of coal. It is also essential that, according to expression (6), the diffusion of methane in the coal seam depends on both the coal grade through the diffusion coefficient of bulk material, and on the dimensional dependence of the coal seam. For the classical case, there is no such dependence on the dimensional factor.

Let's consider, as an example, the first boundary problem, which has the form:

$$\begin{aligned} C(x)\big|_{x=R(0)} &= \frac{\delta_1}{D_0}\cdot\left(R(0)+R(I)\ln R(0)\right)+\delta_2 = C_1, \\ C(x)\big|_{x=R(I)} &= \frac{\delta_1}{D_0}\cdot\left(R(I)+R(I)\ln R(I)\right)+\delta_2 = C_2, \end{aligned} \tag{8}$$

where $R(0)=0.36$ nm. From the system of equations (8) it follows that:

$$C_1 = \frac{\delta_1}{D_0}\cdot\left(R(0)+R(I)\ln R(0)\right)+\delta_2,$$

$$C_2 = \frac{\delta_1}{D_0}\cdot\left(R(I)+R(I)\ln R(I)\right)+\delta_2.$$

By subtracting expression one from expression, we obtain:

$$C_1 - C_2 = \frac{\delta_1}{D_0}\cdot\left[\left(R(0)+R(I)\ln R(0)\right) - \right.$$

$$\left. -\left(R(I)+R(I)\ln R(I)\right)\right] = \frac{\delta_1\gamma}{D_0},$$

$$\delta_1 = \frac{(C_1-C_2)\cdot D_0}{\gamma},$$

$$\delta_2 = C_1 - \frac{(C_1-C_2)\cdot\left(R(0)+R(I)\ln R(0)\right)}{\gamma}.$$

In general, the problem is represented as follows:

$$\begin{aligned} C(x) &= \frac{(C_1-C_2)\cdot D_0}{\gamma}\cdot\left(x+R(I)\ln x\right)+C_1 - \\ &-\frac{(C_1-C_2)\cdot D_0\cdot\left(R(0)+R(I)\ln R(0)\right)}{\gamma}. \end{aligned} \tag{9}$$

The solution in the case of Fick's law will be in the form:

$$C(x) = \frac{(C_1-C_2)}{R(I)}\cdot x + C_1. \tag{10}$$

The comparison of formulas (9) and (10) shows that the methane diffusion of a nanometer-thick coal seam is significantly different from that of a massive sample. Equation (9) can be easily calculated on modern computers when setting the experimental values of the coal seam.

Conclusion

The article proposes a model by which the thickness of the surface layer of coal of the Karaganda basin is calculated. The model is based on the equation in which one fundamental parameter is the molar (atomic) volume of the coal matter. It is equal to the fraction of the molar mass of coal and its density. Currently, it is customary to consider coal as a stable amorphous copolymer consisting of aggregates of monomeric units linked by relatively weak cross-links. We use the work of Moskalenko and others, which shows that such a characteristic as the «molecular weight» of coal, quite well reflects the degree of metamorphism, and is decisive for studying the composition and structure of coal raw materials. Using the formula for calculating the molecular weight of coal obtained in this work and our model, we obtained the thickness of the surface layer of coal in the Karaganda basin of ~150-200 nm. It is 2 orders of magnitude greater than the thickness of the surface layer of metals. This structure is a nanostructure type. This layer possesses physical and chemical properties of nanomaterials: changing the crystal (supramolecular) structure of coal; changing its electronic structure and its electrical conductivity; changing the conditions of the stress state of coal; changing the conditions of methane diffusion in coal seams and many other phenomena.

The article shows how dimensional effects in the coal matter affect the stationary diffusion of methane, which, in the simplest case, is described by the Fick's law. It has theoretically been obtained that the diffusion of methane in the coal seam depends on both the coal grade through the diffusion coefficient of the bulk material, and on the dimensional dependence of the coal seam. For the classical case, there is no such dependence on the dimensional factor.

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Нанометрлік қалыңдықтағы көмірдің беткі қабатындағы метанның диффузиясы

*[1]*МУЛЛАҒАЛИЕВА Лилия Фандусқызы, докторант, m_liliya88@mail.ru,*
[1]БАЙМҰХАМЕТОВ Серғазы Қабиұлы, т.ғ.д., профессор, s.baimukhamet@gmail.com,
[1]ПОРТНОВ Василий Сергеевич, т.ғ.д., профессор, vs_portnov@mail.ru,
[1]ЮРОВ Виктор Михайлович, ф.-м.ғ.к., ҒЗО директоры, exciton@list.ru,
[1]«Әбілқас Сағынов атындағы Қарағанды техникалық университеті» КеАҚ, Қазақстан, Қарағанды, Н. Назарбаев даңғылы, 56,

**автор-корреспондент.*

Аңдатпа. *Қарағанды алабының Шерубайнұра учаскесіндегі көмір қабатының беткі қабатының қалыңдығының ұсынылған үлгісінен бұл қалыңдық 150 нм-ден аспайтыны шығады. Мұндай өлшемдегі наноқұрылымдар үшін көмір қабатындағы микрожарықтар арқылы метанның диффузиялық коэффициентін қоса алғанда, барлық физикалық қасиеттердің өлшемдік тәуелділіктері бар. Бұл Фик теңдеуіндегі метанның диффузиясы үшін диффузия коэффициенті де коллектордың мөлшеріне байланысты болады деп болжау керек дегенді білдіреді. Бұл мәселені шешу нанометрлік қалыңдығы бар көмір қабатындағы метанның диффузиясы массивтік үлгіден айтарлықтай ерекшеленетінін көрсетті. Көмір қабатындағы метанның диффузиясы массивтік үлгінің диффузиялық коэффициенті арқылы көмірдің дәрежесіне де, өлшемдік факторға да байланысты екендігі де маңызды. Классикалық жағдайда мұндай тәуелділік жоқ. Бұл көмір қабаттарының метаморфизмі кезінде, әсіресе олардың тереңдігінің өзгеруі кезінде олардың беткі қасиеттерінің құрылымдық ерекшеліктерін ескере отырып, көмір арқылы метанның диффузия механизміне әсер етеді.*

Кілт сөздер: *наноқұрылым, беткі қабат қалыңдығы, көмір, молярлық масса, шахта, бассейн, коллектор, құрылым, атом қабаты, көміртек, өлшемдік эффект, диффузия, метан, модель.*

Диффузия метана в поверхностном слое угля нанометровой толщины

*[1]*МУЛЛАГАЛИЕВА Лилия Фандусовна, докторант, m_liliya88@mail.ru,*
[1]БАЙМУХАМЕТОВ Сергазы Кабиевич, д.т.н., профессор, s.baimukhamet@gmail.com,
[1]ПОРТНОВ Василий Сергеевич, д.т.н., профессор, vs_portnov@mail.ru,
[1]ЮРОВ Виктор Михайлович, к.ф.-м.н., директор НИЦ, exciton@list.ru,
[1]НАО «Карагандинский технический университет имени Абылкаса Сагинова», Казахстан, Караганда, пр. Н. Назарбаева, 56,

**автор-корреспондент.*

Аннотация. *Из предложенной модели толщины поверхностного слоя угольного пласта на Шерубайнуринском участке Карагандинского бассейна вытекает вывод, что эта толщина не превышает 150 нм. Для наноструктур таких размеров имеют место размерные зависимости всех физических свойств, включая и коэффициент диффузии метана по микротрещинам угольного пласта. Это означает, что для диффузии метана в уравнении Фика нужно полагать, что коэффициент диффузии также будет зависеть от размера пласта. Решение такой задачи показало, что диффузия метана угольного пласта нанометровой толщины значительно отличается от массивного образца. Существенно также, что диффузия метана в угольном пласте зависит как от марки угля через коэффициент диффузии массивного образца, так и от размерного фактора.*

В классическом случае такой зависимости нет. Это сказывается на механизме протекания диффузии метана через уголь с учетом особенностей строения их поверхностных свойств при метаморфизме угольных пластов, особенно с изменением их глубины.

Ключевые слова: *наноструктура, толщина поверхностного слоя, уголь, молярная масса, шахта, бассейн, пласт, структура, атомный слой, углерод, размерный эффект, диффузия, метан, модель.*

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