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Research Article

# The Effect of the Adsorbed Phase of Methane on its Mass Transfer in the Elastic Area of the Rebuff Pressure of the Coal Seam

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## Abstract

The article investigates the process of filtration of methane in the elastic area of the rebuff pressure of a gas-saturated coal seam, taking into account the adsorbed methane. The calculation of the possible degree of filling the pores of the disturbed zone of the coal seam with adsorbed methane according to its entropy was calculated. The calculation showed that the state of the thermodynamic system adsorbed gas-microporous coal space is most likely energetically with a degree of pore filling with methane by 40%. In this regard, when filtering free methane in a coal seam as a result of a pressure drop between its free and adsorbed phases, additional coal saturation with adsorbed methane can occur. As a result, it was determined that as the support pressure reaches the disturbed zone max, this volume can increase. This will lead to a decrease in the gas pressure in the filtration stream of free methane and will create a "reservoir" with a significant amount of methane adsorbed on the border with the inelastic area.

## Introduction

Currently, in geomechanics associated with the development of highly efficient technologies for the extraction of coal and coal mine methane, the most urgent task is to establish patterns of diffusion-filtration flows of methane mass transfer in the coal-rock mass [1-3]. One of the most important areas in the massif of mining is the elastic area of the rebuff pressure, which predetermines the state of methane in the bottomhole zone of the coal seam and thereby the regularities of its release into the developed space. For many years, it was believed that since this area is subject to increased rock pressure, then, a priori, the mass transfer of methane is largely blocked due to the implementation of a compression mechanism for deforming the structure of coal [4-5]. However, data from recent studies show that this mechanism and the state in the structure of coal methane is more complex [5-10]. For example, the elastic area of the rebuff pressure is characterized by competing processes of compression-decompression of the coal structure, determined by the mechanical properties [5-7], and the diffusion of methane in the coal can develop not only through various channels in the microporous structure, but also perpendicular to them. solid-state diffusion [9]. In addition, against the background of such complex macro transfer processes in the elastic area, it is necessary to take into account the two-phase state of methane free and sorbet [9]. Accounting for adsorbed methane, according to Langmuir's ideal theory [10], which is currently mainly used in geomechanics, treats this gas in a state of quasi-static equilibrium outside the processes occurring in the methane-coal system when its equilibrium state is violated. In this case, the pressure is considered only as the pressure of free methane, and the energy relationship of methane with coal, which determines the activation of sorption-desorption processes in the coal seam, is not taken into account. In this regard, the goal was set: to establish the effects of the adsorbed methane phase on its methane transfer in the elastic pressure bearing region, taking into account modern data on the state of adsorbed methane in the microporous structure of the coal seam and its relationship with the filtration flow of free methane.

## Methods

### Assessment of the state of adsorbed methane in the micropores of coal

One of the main parameters in the simulation of processes associated with the assessment of the disturbance of the equilibrium state of a coal seam saturated with free and sorbet methane is the pressure of methane adsorbed in the coal. In numerical calculations related to the adsorption of methane, one usually uses the concept of reduced pressure, which is understood to be the pressure of a gas transferred from an adsorbed state to a free state-p. In this case, calculations are made considering the gas in the pore space as ideal. At the same time, the inclusion of sorption forces is neglected, while, under the pressure of adsorbed methane in the micropores of coal, we mean the pressure due to the force field of the intermolecular interaction of methane with the pore walls. The most fully take this into account allows Hill's equation of state, which has the form [9]:

$$\ln p = \ln \frac{\theta}{k_1(1-\theta)} + \frac{\theta}{1-\theta} - k_2\theta \quad (1)$$

where  $\theta$  is the degree of pore filling with methane;  $k_1^{-1} = k_1 b_2$ ;  $k_1$  is the Henry constant determined by the potential energy of interaction of gas molecules with the pore wall  $U(r)$  located at a distance  $r$ ;  $k_2 = 2a_2 / (b_2 RT)$ ;  $a_2$ ,  $b_2$  --- constants characterizing interactions between molecules;  $R$  is the gas constant;  $T$  is the temperature.

From the formula (1) we can see that the main variable parameter, in specific mining and geological conditions, determining the pressure of adsorbed methane  $p$  is the degree of filling of the pores of methane  $\theta$ . In this regard, the work assessed the effect

of this parameter on the entropy [11] of methane adsorbed in a coal seam. As a result, the following equation for entropy was obtained:

$$S = S^0 - \frac{H}{T} - R \ln P = C_v \ln(T) + R \ln(\theta) + R \left( \frac{\partial \ln k_1}{\partial T} \right)_\theta + R \ln(k_1) - R \ln \frac{\theta}{1-\theta} - R \frac{\theta}{1-\theta} \quad (2)$$

where  $S^0$  is the entropy of an ideal gas;  $H$  is the enthalpy of sorbed methane;  $C_v$  is the molar heat capacity of methane;  $T$  is the formation temperature;  $R$  is the gas constant. The results of the calculation of the entropy factor  $TS$  from the degree of filling of the pores with methane are presented in Figure 1. As can be seen from this Figure, the entropy factor has a maximum value, when the degree of filling of the pores with methane is 0.40. This means that saturation of the pores with methane has high probability, therefore, more advantageous energetically. That is, when the coal seam was in the elastic area of the rebuff pressure, the porous space of the coal is filled with adsorbed methane, about 40% with very strong sorption forces, whose energy is 10-20 kJ/mol [9].

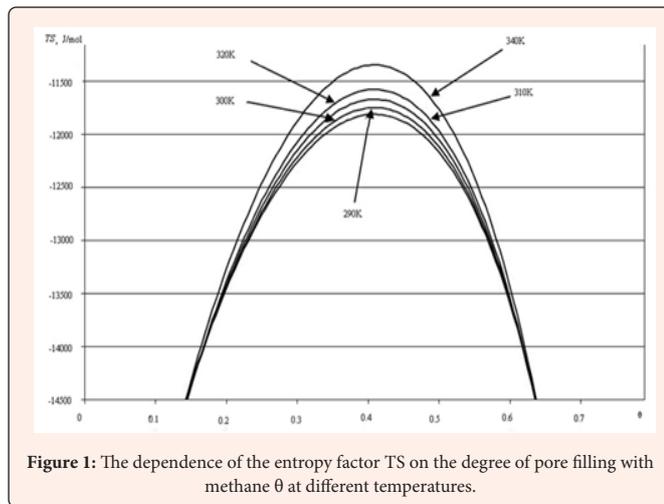


Figure 1: The dependence of the entropy factor  $TS$  on the degree of pore filling with methane  $\theta$  at different temperatures.

**Determination of the main parameters of the elastic area of the rebuff pressure and filtration laws in it free methane**

The nature of the interaction of adsorbed methane with free will be determined, first of all, by the stress state of the coal seam in the elastic area of the rebuff pressure. These parameters were determined by the known fundamental formulas of *Petukhov I & Linkov A* [12], obtained taking into account the large amount of static data on the strike of the zone of the rebuff pressure. As an example, the mining and geological conditions of the Pokrovskiy District of Donbass were considered. The results of the calculation of the vertical stresses  $\sigma_y(x)$  and the potential energy  $U^p(x)$  of deformation are presented in Figure 2. The results of the calculations, as can be seen from the graphs obtained in Figure 1. It is showed that there is no zone of disintegration at max of the rebuff pressure in the considered geological conditions. In assessing the possible implementation of the filtration process of free methane in the elastic zone of the coal bed bearing pressure, they were based on the formation of the reservoir as a structurally inhomogeneous system in the form of combinations of several sections located in different zones of the rebuff pressure. Each of these areas was described by average values of porosity and gas permeability, which were determined by the well-known method *K Basniev* [13,14]. This allowed for each combination of sections of the reservoir to use the equations of *L. Leibenzon* for non-stationary isothermal one-dimensional gas filtration [15]:

$$\frac{\partial p}{\partial t} = \frac{kp}{2\mu m} \cdot \frac{\partial^2 p^2}{\partial x^2} \quad (3)$$

where  $p$  is the current gas pressure in the reservoir;  $t$  is time;  $k$  is the gas permeability of the coal seam;  $m$  is the porosity of coal;  $\mu$  is the dynamic viscosity of the gas.

When solving equation (3), an approximate solution was used by *Zhelтов Y* [15] in the form of:

$$p^2(x,t) = A \cdot \frac{x}{L(t)} - \frac{A}{2} \cdot \frac{x^2}{L^2(t)} + p_u^2 - \frac{A}{2} \quad (4)$$

where  $p_u$  is the gas pressure in an intact formation;  $A=2(p_u^2 - p_a^2)$ ;  $p_a$ -gas pressure at the bottom;  $L(t)$  is the boundary of the perturbation zone of methane pressure in the coal seam.

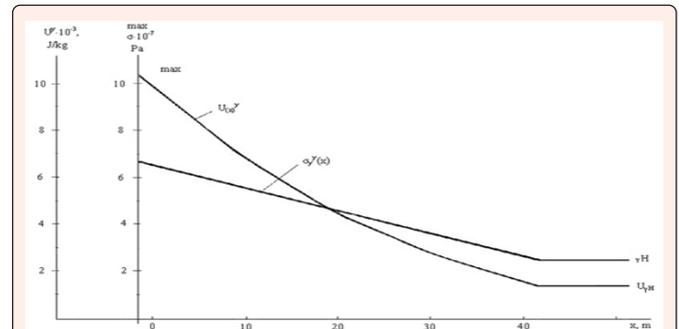


Figure 2: Patterns of changes in the basic parameters that determine the initial state of the coal seam in the elastic area of the rebuff pressure, where  $\gamma$  is the volume weight of rocks containing a coal rock;  $H$ -the depth of the reservoir;  $\sigma_y(x)$ ,  $U_y(x)$ ,  $U_yH$  are respectively the main normal stresses, the potential deformation energy in the elastic area of the rebuff pressure and in the rocks.

The boundary conditions had the form:

$$p = p_a \text{ at } x=0 \text{ and at } p=p_u \text{ at } x=\infty; \quad \frac{\partial p}{\partial x} = 0 \text{ at } x = L(t). \quad (5)$$

Gas permeability was established by known formulas *Petukhov I & Linkov A* [12]. Numerical calculations of the distribution of pressure of free methane according to the above algorithm were carried out for mining and geological conditions Pokrovskiy district of Donbas. The results of calculating the distribution of methane in the elastic area of the rebuff pressure are shown in Figure 3.

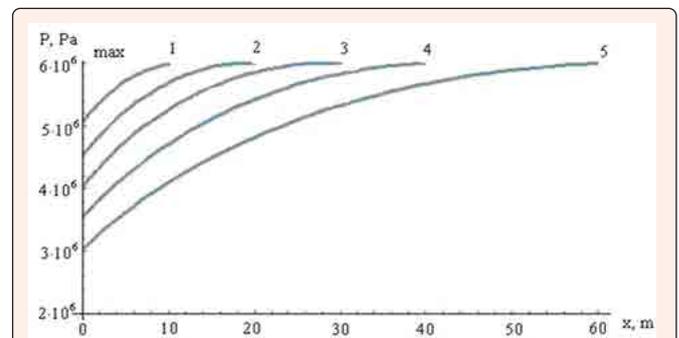


Figure 3: Patterns of change in pressure of free methane in the elastic area of the rebuff pressure of a structurally inhomogeneous coal seam of the elastic area of the rebuff pressure at different fixed points in time: 1- $t=0.6 \cdot 10^3$ s; 2- $t=1.1 \cdot 10^3$ s; 3- $t=1.9 \cdot 10^3$ s; 4- $t=0.35 \cdot 10^4$ s; 5- $t=0.7 \cdot 10^4$ s.

**Results and Discussion**

On the basis of the regularities established above, the increment of the potential energy of the macro- and microstructure of coal subjected to deformations in the elastic zone of the rebuff pressure was calculated. It was taken into account that the rigidity of the molecular skeleton of coal is 5 times higher than the rigidity of its macrostructure [9]. As a result, dependences of the potential energy increment were obtained, which are shown in Figure 4.

Analysis of the calculations showed that the increment of the potential energy of the molecular structure of coal is less than the corresponding parameter for the skeleton of the macrostructure of coal by one orders of magnitude. If we take into account that the energy of the conformational rearrangements of the molecular structure of coal is in the range of  $10$  to  $10^5$  J/mol [9], then it can be concluded that the stresses in the elastic zone of the rebuff pressure have little effect on the deformation of the molecular structure of coal. Therefore, the processes of compression-decompression of the molecular structure of coal will be determined only by the initial potential of the molecular structure of coal, which is characterized by a certain distribution of the energy of conformational rearrangements.

To assess the processes of hardening-softening of the microstructure of coal in the elastic area of the rebuff pressure, we used the interconnection of the energy of conformations with the increment of interlayer distances in the molecular structure of coal [9], shown in Figure 5. From this Figure, not exceeding 170 kJ/mol, the molecular structure of coal of all degrees of metamorphism is confirmed only by decompression processes characterized by an increase in interlayer distances. When the potential energy becomes greater than this value, some characteristic alternating peaks appear on the graphical dependencies. They describe the transition of the decompression deformation process into a compression one and vice versa.

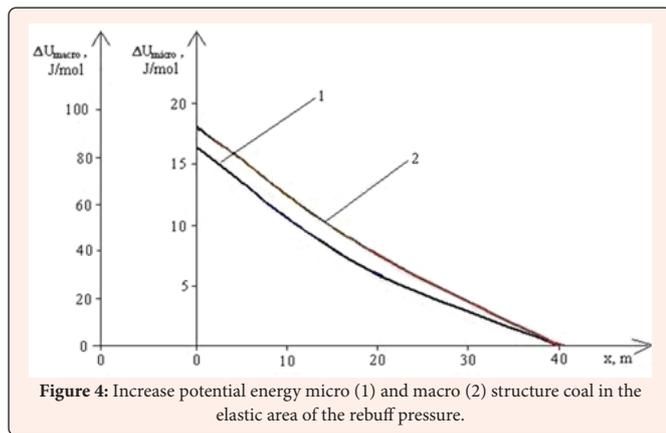


Figure 4: Increase potential energy micro (1) and macro (2) structure coal in the elastic area of the rebuff pressure.

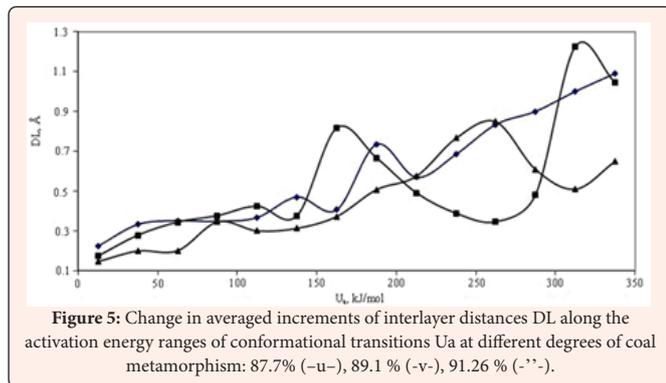


Figure 5: Change in averaged increments of interlayer distances DL along the activation energy ranges of conformational transitions  $U_a$  at different degrees of coal metamorphism: 87.7% (-u-), 89.1% (-v-), 91.26% (-''-).

Thus, the first peak on these curves for low and medium degree metamorphism coals appears in the range of activation energies of 150-175 kJ/mol, without reaching the energy of breaking the valence bonds, which amount to 250-350 kJ/mol. The second peak is already located in the region corresponding to the valence bond breaking energy. In the case of coal of a high degree of metamorphism, the initial maximum is reached in the region of the activation energy  $U_a=250$  kJ/mol. Such a character of the process of rearrangement of the structural chains of a coal substance with a change in the energy potential of the molecular structure indicates that the microstructure of coal of low and medium degrees of metamorphism compared with coal of a high degree of metamorphism is more sensitive and susceptible to changes in external technological impact. In this case, the region of 150-200 kJ/mol, where the interlayer distance begins to grow very sharply without breaking the valence bonds, can be considered a zone of constructive conformational rearrangements causing the activation of methane diffusion, its adsorption and desorption in the absence of mechanical destructive processes in the microstructure of the coal array. Thus, the energy potential of the elastic area of the rebuff pressure, due to the stress-strain state in this zone will not have a significant impact on the molecular structure of coal. From this it follows that the mass transfer of methane in the elastic area will take place. The study of the mutual influence of the phase components of methane on its transfer in the elastic area was carried out for a more disturbed zone of a structurally inhomogeneous coal seam, characterized by a large porous space capable of containing a large volume of adsorbed methane. For this, we took advantage of the above-established laws of change in pressure of free methane when it was filtered in a coal seam, shown in Figure 3, which showed the following.

Due to the fact that when a coal seam enters an elastic pressure field, it is saturated with adsorbed methane, as stated above, by only 40% when moving the area under study

in an elastic pressure field, as a result of pressure drop at its boundaries adsorption and filtration of free methane, during its diffusion, the process of adsorption of methane will be realized. This process will stop either when the maximum possible degree of saturation of this zone with methane in the elastic area occurs, or when the zone moves to the limiting region of the rebuff pressure, which is characterized by unloading of the coal massif. The numerical values of the pressure drops of free methane at the boundary of the violated zone, minus the free gas pressure, can be considered the saturation pressure of adsorption. The values of this pressure as the violated zone moved to the maximum of the rebuff pressure were established numerically on the basis of the laws of filtration of free methane in the elastic area, shown in Figure 3. The results of the calculation are shown in Figure 6.

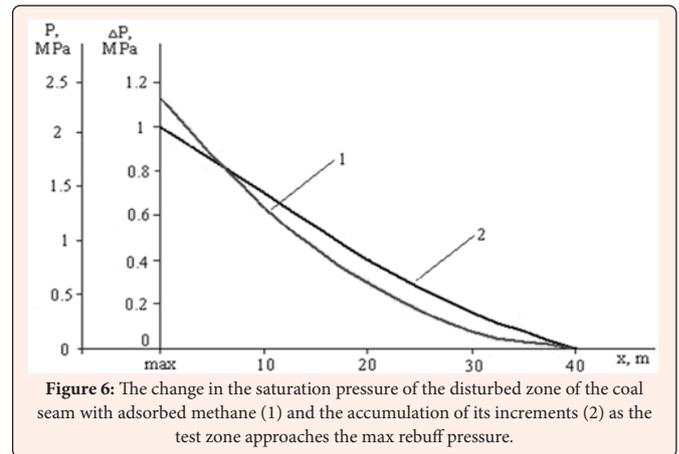


Figure 6: The change in the saturation pressure of the disturbed zone of the coal seam with adsorbed methane (1) and the accumulation of its increments (2) as the test zone approaches the max rebuff pressure.

As can be seen from Figure 6, the increment of the saturation pressure of the disturbed zone is carried out according to a linear law, and the change in the total saturation pressure as it approaches the maximum of the rebuff pressure can be approximated by the following relationship:

$$P=5.7-1.5 \ln (x+10); [P]=\text{MPa}, (6)$$

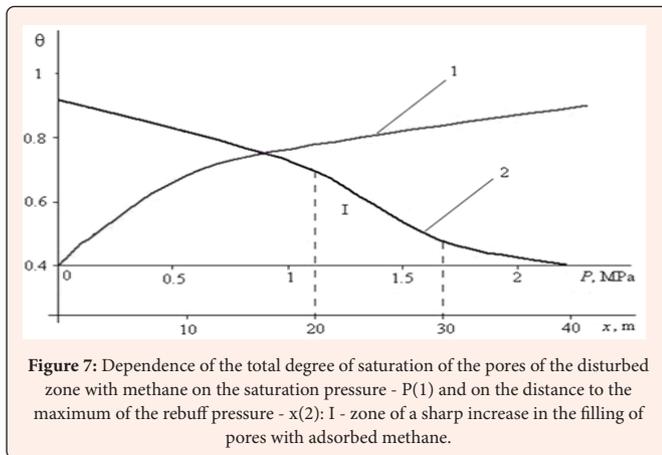
where  $(x+10)$  – distance from the place in the elastic area to the beginning of working tunnel.

The approximating dependence (6) can be used in estimating the volumes of adsorbed methane by the displaced area of the disturbed zone at any distance from the bottom of the mine. In general, as follows from Figure 6, by the time the disturbed zone approaches the maximum of the rebuff pressure, it was saturated with methane, the pressure of which was 2.3 MPa. The degree of saturation of the pores with methane was determined on the basis of the Hill (1) ratio, which describes the dependence of the pressure of methane adsorbed by coal with the degree of filling of the pores with gas, taking into account the experimental adsorption isotherms established for coal samples [15]. Within the limits of the above general increment of methane pressure during its adsorption in the disturbed zone, equal to 2.3 MPa, to calculate the degree of additional saturation of pores with methane, we used the linear part of methane adsorption isotherms, which were approximated by the Hill equation in the form

$$\Delta P = \frac{\Delta \theta}{b_2 k_1 (1 - \Delta \theta)} ; [\Delta P] = \text{MPa}, (7)$$

where for coal, the approximation coefficients are:  $b_2=0.88$ ;  $k_1$ , taking into account that the structure of the coal is broken, is 1.01,  $\Delta P, D_s$ - increase  $\Delta P$  and  $\Delta \theta$ .

Thus, we obtained an approximating dependence of pressure on the degree of pore filling with methane in the form of (7), which takes into account the square area of the adsorbent, the energy of sorption interaction of methane with coal, and the degree of pore filling with methane. The results of the calculation of the total degree of filling of the pores with adsorbed methane  $\theta$  depending on the saturation pressure, as well as the change in the total volume of this gas as the maximum of the rebuff pressure approaches the disturbed zone, are presented in Figure 7.



As can be seen from the graphs presented in Figure 7, the saturation of pores with adsorbed methane most intensively occurs in the initial period of entry of the investigated area into the elastic area, when  $P < 1$  MPa. This is evidenced by the pattern of changes in the degree of saturation of coal with adsorbed methane, depending on the distance to the maximum of the rebuff pressure. A sharp burst of coal seam saturation with methane occurs at a distance from an intact coal massif (10-20 m). This is apparently due to the fact that no significant compaction of the fractured macrostructure of coal has occurred in this zone. The overall degree of saturation of the microporous space of coal, taking into account its initial saturation by 40%, as can be seen from Figure 7, was 93%. That is, when approaching the inelastic area of the rebuff pressure, the coal seam will be a reservoir with a significant amount of methane associated with coal with very strong intermolecular bonds, the energy of which is 10-20 kJ/mol. Thus, as a result of the studies performed on the effect of the sorbed phase of methane on its mass transfer in the elastic area of the rebuff pressure, the following conclusions were made.

### Conclusion

- As a result of calculating the entropy of methane adsorbed in a coal seam, it was found that the state of this system is most likely, and, therefore, more beneficial energetically, with a degree of pore filling with methane about 40 % for any depth of coal seam. Therefore, in the elastic area of the rebuff pressure, during filtration-diffusion processes as a result of the pressure drop of free and adsorbed methane, the process of adsorption of methane by coal can be realized.
- The most active process of adsorption of methane by coal in the elastic area of the rebuff pressure is realized near the border with an intact coal mass. The increase in its volume occurs according to a logarithmic law and in some mining and geological conditions it can reach the value of the maximum sorption gas intensity of the microporous space of a coal seam.
- The effect of the adsorbed phase of methane on its mass transfer in the elastic area of the rebuff pressure of the coal seam is as follows. The main volume of methane in this area can be transferred not only by the filtration process, but also by the microporous structure of the reservoir, saturated with adsorbed methane, as it moves to max bearing pressure. In this regard, when unloading the reservoir in the inelastic area, methane can be released in large volumes. It is unsafe in mining. Therefore, it is advisable to degas the adsorbed methane in the elastic area of the rebuff pressure.

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