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### METHANE PHASE IN FOSSIL COALS UNDER PRESSURE

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Coals in nature are produced as a result of intricate processes, in which biological, chemical and tectonic factors exert (under conditions of high pressures and temperatures) prolonged influence over plant debris. Molecules of cellulose, the major part of plant cells, lose a considerable part of hydrogen and oxygen, i.e., their material, in the form of water, methane and carbon dioxide. Parallel to this polymerization and condensation of molecules, resulting in cyclic compounds with side chains, containing functional groups, takes place. The number of groups is decreased as metamorphic transformation in the form of chemical and physico-structural processes goes on. The main agent for chemical metamorphism is heat. It produces the intricate molecular whole of fossil coals. Pressure of rock and emitted gaseous products are responsible for the distinctive dispersed structure of pores and cracks, i.e., physico-structural metamorphism. Vacancies in coals (pores and cracks) play an important role, not to be underestimated. Structurally they form a hierarchy of levels and groups, properties of which differ very considerably.

The forms of methane in fossil coals. The problem of types of vacancies in fossil coals is connected with the problem of methane distribution in them and forms, in which methane is found in coals.

Depending on the size of vacancies, gases of coals can be in different states: free, adsorbed and absorbed (solid solution). Free and adsorbed methane fills macropores, mesopores, cracks and interblock intervals. The absorbed methane is in intermolecular spaces of coal substance. We investigated experimentally and theoretically the behavior of methane (both in the absorbed form and in solid solutions in coal organic substance) under pressure, i.e., in conditions reproducing natural conditions of coals. The pressure of gases in hazard mines of Donbas at 800 metres below the surface (which corresponds to the rock pressure of  $10^7$  Pa) according to measurements is ca.  $(10-120) \cdot 10^5$  Pa [14].

Methane in solid solutions (model description). Recently physical, physical-chemical and coals petrographic investigations [1,2] showed that in coal vitrinites polymer substances with linear and bifurcated macromolecular structures of globular shape are present even with abundance of linear fragments. According to estimates [3] graphitoids account for 40 ... 60% of coals and 60 ... 85% of anthracites, the rest is linear-polymerized carbon. Thus, the modern view (and sufficiently general) at coals represents them as a complicated system of graphite-like crystals with polymer interlayers. The fundamental properties of the latter are due to spatial arrangement of atoms and atomic groups of polymer chains, i.e. so called conformations of coal macromolecules. It is to be noted here that since it concerns spatial dimensions and multiple chains of considerable size, the main method of theoretical consideration of conformational properties is to be taken from the classical statistical mechanics.

To deal with coal substance studies in the framework of this model we must take into consideration gases and other fluids, which are distributed in coals due to their origin conditions ( $\text{CH}_4$ ,  $\text{CO}_2$ , heavy hydrocarbons, etc.). It is to note that solubility coefficients of gas in crystallites and polymer interlayers differ, at least, by the order of magnitude. Methane molecules easily penetrate in the loose structure of polymer interlayers, but with great difficulty into the densely packed carbon layers of crystallites. Moreover, at the interface of crystallites and polymers interlayers additional mechanical stresses take place due to superfluid concentration of solved gases (osmotic pressure).

The polymer gas-coal solid-solution model (PGCSS-model) proceeds from the model by P. Flori, published forty years ago [4]. The starting point for P. Flori is the approximation of self-consistent field. His model is formulated in the framework of the lattice model for a polymer chain.

Let a system (PGCSS) includes  $N_1$  polymer molecules of coal substance and each molecule includes  $r$  chains plus  $N_2$  monomer gas molecules (or of some other fluid). Then in the hypothetical lattice representing PGCSS the  $N_0$  sites are occupied:

$$N_0 = N_2 + rN_1.$$

Each molecule of solved substance occupies one site in the lattice, each molecule of polymer occupies  $r$  sites. We assume that a polymer chain is flexible and contains  $r$  movable segments. Thus, one segment of the molecule being fixed, another occupies one of the neighbor free sites of the lattice. The flexible polymer molecule might have different configurations, and in case of the fixed configuration might have different orientations relative to the lattice.

Entropy variations, when monomer gas molecules are solved in the coal polymer, are written as

$$\Delta S = -kN_0 \left\{ \varphi \text{Ln} \varphi + \frac{1-\varphi}{r} \text{Ln}(1-\varphi) \right\}, \quad (1)$$

where  $\varphi$  — part of lattice sites, occupied by molecules of solved gas is  $\varphi = N_2/N_0$ ; and variations of inner energy are as follows

$$\Delta E = kN_0 T(\varphi\chi - \varphi^2\chi). \quad (2)$$

The free energy  $F$  of PGCSS according to this model varies in the general form as:

$$\Delta F = \Delta E - kT\Delta S = kN_0T\left\{\chi\varphi - \chi\varphi^2 + \varphi\ln\varphi + \frac{1-\varphi}{r}\ln(1-\varphi)\right\}. \quad (3)$$

Thus, in the framework of our model the volume interactions are characterized by unique nondimensional value  $\chi$ , which is called the Flory-Huggins parameter. At  $\chi = 0$  energy interactions in the polymer solution are not observed, the only agents are the forces of steric repulsion between chain links. This is the case of so called athermic solutions.

**The stress of swelling.** Swelling of fossil coals is observed as the result of absorption of gases ( $\text{CH}_4$ ,  $\text{CO}_2$  etc.). This phenomena is investigated in great detail [2-4]. In the framework of our model it obtains a natural description and the derived formula can be used to determine some characteristics of coal seams, which are inaccessible for direct measurements. One of such characteristics is the excessive stress  $\sigma$ , at the interface "graphite-like crystallite polymer interlayer" due to a more intensive solubility of gases in polymer interlayers in comparison with solubility in crystallites. Penetration of gas (or other fluid) molecules in coal polymers results in variations of the free energy in the system. One of the consequences of this is the excessive pressure affecting the external boundary of the system, which can be obtained registered, e.g., by a laser with an external movable mirror [2,3]. This technique was developed in Moscow Mining Institute. PGCSS-model permits to calculate values of swelling stresses in nonaromatic interlayers:

$$\sigma = -\frac{kT}{a^3}\left\{\varphi - \frac{1}{r}\left[\ln(1-\varphi) + \varphi\right] - \chi\varphi^2\right\}, \quad (4)$$

where  $k$  is the Boltzman constant,  $a$  is the parameter of the hypothetic lattice, which defines the polymer structure of coal interlayers, depending on the stage of metamorphism of coal substance,  $T$  is the temperature of the coal seam in Kelvin degrees,  $r$  is the number of chain links in a polymer molecule. There is one more characteristic, namely, nondimensional parameter  $\chi$  presenting energy and describing interactions between different molecular groups. The degree of saturation of coal layers by methane is characterised by the nondimensional concentration of methane molecules in coal. It is determined with the aid of NMR spectra for gas-saturated coals.

By equalizing the chemical potentials of the free gas and the gas in PGCSS we obtain the relation for determination of  $a$ :

$$a^3 = \frac{T}{r}\ln\left(\frac{P\lambda^3}{TZ}\right), \quad (5)$$

where  $P$  — is the pressure of the free gas, with  $\lambda^3$  — as the quantum volume and  $Z$  — as the inner statistical sum of the gas molecule.

The important characteristics of the swelling process are swelling stresses, localized at the disclosed (free) interface of coal. Since the graphite-like inclusions and polymer non-aromatic interlayers merge with the interface (they are saturated by gas molecules), the swelling stresses  $\sigma_{fr}$  are proportional to the fraction of these interlayers  $(1 - f_a)^{2/3}$ :

$$\sigma = \frac{kT}{3}(1 - f_a)^{2/3}\ln\left(\frac{1}{\varphi} - 1 - \chi\right), \quad (6)$$

where  $f_a$  is the degree of aromatic fractions in coal, determined by the X-ray data. The parameters  $f_a$ ,  $\chi$ ,  $a$ ,  $r$  are determined for every mine by measurements and

consequent calculations using the adopted methods for the corresponding standard samples.

Thus, the carried-out investigations allow to develop the methods of determination of excessive stresses in gas-coal solid solutions.

The preliminary estimates show that, e.g., in coals under study of grade *K* ( $a \approx 10^{-9}$  m,  $\chi \approx -20$ ,  $t \approx 30^\circ\text{C}$ ,  $T = 303$  K), at the methane concentration  $\varphi \approx 0.01$  the excessive stresses are estimated as:  $\sigma \approx 10^4$  Pa.

The swelling stress  $\sigma$ , formed in gas-saturated coals and localized at the interface of graphite-like crystallites is the additional factor of instability of coal layers under conditions of the varying rock pressure at the zone of mine working the uncompensated swelling stresses initiate the destruction of the coal seam. Thus the value of the computed swelling stress  $\sigma$  can serve as the characteristic of inclination of the coal to destruction.

The adsorbed methane. NMR is the best method for investigations of mobility of fluid molecules in the fixed matrix. It reveals mobility of protons in different energy levels in comparison with hydrogen atoms in free fluids. These levels are recorded as NMR spectra.

In our case the role of the matrix plays the organic constituents of coals. At NMR spectra it is represented by the wide line ( $\Delta H_1 = 300-500$  A/m). The width of the methane line in the solid solution is of the same order of magnitude as  $\Delta H_1$  i.e., the solid solution contributes to the wide line of the spectrum. However, since the methane, solved in organic constituents of coal forms the thermodynamic balance with the methane sorbed at the surface inside voids, the narrow line of the spectrum ( $\Delta H_2 = 8-80$  A/m) representing the adsorbed methane might give information as to the methane amount in the solid solution. Since coals of different grades differ in relation to sorption of methane, we investigated behavior of the absorbed methane in coals at the different stage of metamorphism at the sorption plant, equipped with the high-pressure system for pressure variation in the range 0.1-8 MPa. NMR spectra were taken by the NMR-spectrometer of  $^1\text{H}$  wide lines. At pressure rise a tendency to more narrow lines at spectrograms was observed. For coals of grade *T* at  $P = 0.1$  MPa  $\Delta H_2 = 33.4$  A/m and at  $P = 6.0$  MPa  $\Delta H_2 = 14.3$  A/m was obtained. For coals of grade *K* the data were: at  $P = 0.1$  MPa  $\Delta H_2 = 38.9$  A/m, at  $P = 6.0$  MPa,  $\Delta H_2 = 18.3$  A/m.

This means that every next layer of methane molecules is in the more free state.

The width of line  $\Delta H$  for the adsorbed methane (23.8-71.6 A/m) is some orders of magnitude greater, than for the free methane ( $8 \cdot 10^{-3}$  A/m) [5]. This allows to assume that  $\text{CH}_4$  molecules are localized in the vicinity of the surface of a solid and execute the translational movements along this surface, i.e., they represent "two-dimensional gas".

In order to answer the question, are the observed lines at NMR spectrograms for the absorbed methane true ones we investigated coals of the following grades: anthracite *A* (Mine after Kiselev, PO Torezanthracite), lean coal, grade  $T_{\text{HB}}$  (hazard — free coal seam, mine Krasny Oktyabr', PO Ordjonikidzeugol'); lean coal, grade  $T_B$  (hazard — liable coal seam, PO Donetskugol'); lean coal, grade  $T_{\text{HB}}$  (coal after a hazardous event, the same mine); line, baking coal, grade *OC* (Mine Sotsialisticheskij Donbas, PO Donetskugol'); coking coal, grade  $K_B$  (hazard-liable coal seam, Mine after Bazhanov, PO Makeevugol') coking coal (after a

hazardous event, the same mine), fat coal, grade Ж (Mine after Tchesnokov, PO Stakhanovugol').

Coal samples were crushed (size 0.5–1 mm) and poured into thin-walled test-glasses, 3 mm diam. Then the samples were put into the high-pressure chamber. After the preliminary vacuum treatment for two-three hours the samples were saturated with methane at  $P = 0.2$  MPa for seven days.

The obtained results representing the widths of lines for the absorbed methane in NMR spectra are summarized in Table

Coal grade	A	$T_{HB}$	$T_B$	$T_{IIB}$	OC	$K_B$	$K_{IIB}$	ZH
$\Delta H_2$ , A/m	27.9	44.6	51.7	45.4	54.1	74.0	65.2	76.4

Our experiments show that the strength coupling of methane molecules-solid substance depends on the coal grade. This is shown by variations of values, representing the width of lines in NMR spectra of methane-saturated coals.

In Fig. 1 NMR spectrograms for methane-saturated coals are shown (grades A(a), T(b), and ZH(c)). It is seen that the intensity of NMR-spectrum of the sorbed methane is maximal for anthracite samples, which proves the greater sorption characteristics of anthracite. Lean coals are less effective at sorption, and fat coals are the least effective of all coal grades. This is explained by the porosity of coals. Coals of grade ZH possess the least sorption volume, and anthracites are in possession of the maximal sorption volume. From all coals under investigation the width of  $\Delta H_2$  — line is the largest for fat coals as they contain the greatest quantity of side

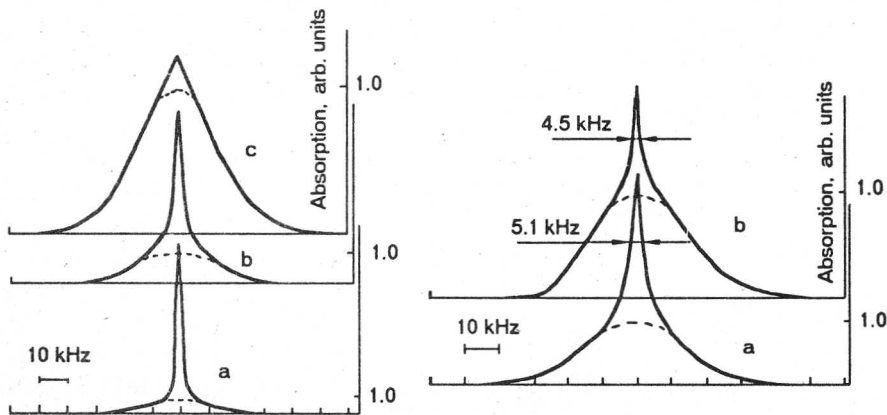


Fig. 1.  $^1\text{H}$  NMR spectra of degassed and methane-saturated coal samples: a — coal samples of grade A, b — coal samples of grade T, c — coal samples of grade ZH, dotted line-spectra of degassed coal samples, solid line-spectra of methane-saturated coal samples

Fig. 2.  $^1\text{H}$  NMR spectra of degassed and methane-saturated coal samples: a — coal samples of grade K from a hazardous region, b — coal samples of grade K after the outburst, dotted line-spectra of degassed coal samples, solid line-spectra of methane-saturated coal samples



aliphatic groups, playing the role of the centers of methane absorption. As for anthracite samples the process of transformation to coal in them is over, aliphatic groups are scarce and adsorbed molecules occupy the volume of pores, which are arranged between carbon sublattices. Since these sublattices occupy practically the whole inner sorption surface of anthracite samples, the number of adsorption centers here is small. Therefore the absorbed molecules in them are more inclined to motion in comparison with molecules, absorbed on aliphatic interlayers. Thus, the line of methane, adsorbed on anthracites, is narrow.

In our investigations data are obtained, which witness the variation of the coupling methane-coal after the methane outburst (see Table, samples 3,4,6 and 7, and also see Fig. 2). Coals before outburst show a wider methane line compared with coal samples after outburst. This confirms conclusion of paper [6].

The authors of this paper conclude that during an outburst a number of final groups are broken. Since the groups play the role of sorption centers, mobility of methane molecules is increased.

In Table samples 2, 3 and 4 of coals grade *T* are given, possessing  $\Delta H_2$ -lines of different width. This is the proof of difference as to the number of absorption centers in case of these samples. Lean coal samples from the hazard-free coal seam and coal samples after the outburst possessing the alike  $\Delta H_2$ , and sample 3 (hazard dangerous coal seam) possesses  $\Delta H_2$ , which is 7.9 A/m higher. This means that in sample 3 more radicals (side groups) are available. In [7] with the aid of EPR-technique it was found that coals, inclined to outbursts, possess more free radicals. Increase of the width of the methane line in NMR spectra for hazard-gangerous coals confirms this conclusion.

Free methane in closed pores. As it was said above free gases occupy pores and cracks. To estimate the amount of free gas in coals we need a more exact estimation of the pore volume.

Pores in coals, as in other solids [8], can be classified as open pores, i.e., such voids and samples, which open outside, and closed ones, which do not open outside. Such classification considering that gas molecules can migrate in closed pores only by means of solid-body diffusion might seem to be artificial. However, it is supported by the considerable difference in diffusion coefficients:  $D_G \geq 10^{-4} \text{ cm}^2/\text{s}$  in the most narrow open channels and  $D_S \approx 10^{-9} \dots 10^{-8} \text{ cm}^2/\text{s}$  in case of solid-body diffusion.

The methods, proposed for determination of differential porosity of fossil coals (according to pore sizes: micropores, of transitional size, submacropores, macropores) as well as of the general volume of pores allow to estimate only the volume of open pores per unit of the coal mass. This is seen by the scale of the obtained values, namely  $0.1 \text{ cm}^3/\text{gr}$  (see, e.g., [9,10]). In fact, comparison of values for specific volumes of fossil coals of different grades with the value for high-density pyrolithic graphite (spec. vol.  $0.5 \text{ cm}^3/\text{gr}$ ) indicates that the summed-up pore volume per unit of the coal mass might vary in the range of  $0.1 \text{ cm}^3/\text{gr}$ – $0.3 \text{ cm}^3/\text{gr}$ , i.e. exceeds the value of the open porosity of fossil coals. The results of investigations with the aid of electron microscopy allow to estimate the linear sizes of these pores as  $10^{-7}$  and  $10^{-4} \text{ cm}$  and, consequently, the number of them per unit of the volume of coal (ca.  $10^{11}$ – $10^{20} \text{ cm}^{-3}$ ). The method of estimation of the closed pore volume was proposed by Alexeev and Sinolitskij [11,12]. It is based on the model of absorption and release of gases by solids with pores. According to this

model gas absorption takes place by rapid penetration of gas molecules via the system of filtration channels into the solid with the consequent diffusion of them over the whole of the solid. The process of solid-body diffusion is the most slow one. It contributes little to gas filtration; however, it defines the regular character of sorption processes. The experiments carried out at coal samples, put into the sorption sample with the fixed initial pressure of gas  $P_0$ , allowed to find availability at least two times of relaxation:  $\tau_1$  of the order of magnitude of several minutes and  $\tau_2$  of the order of magnitude of several days. The estimates associate  $\tau_1$  with the kinetics of filling the open pores as well as of a certain number of closed pores in the vicinity of the external surface of coal samples, and  $\tau_2$  associated with filling in of the closed pores. The variation of pressure in the sorption ampule with time  $t$  might be approximated by the following expression:

$$P(t) = P_{\infty} + A_{\exp}\left(-\frac{t}{\tau_1}\right) + B_{\exp}\left(-\frac{t}{\tau_2}\right), \quad (7)$$

where  $P_{\infty}$  is the balanced pressure,  $A$  and  $B$  are the constants with dimensionality of pressure depending also on the characteristics of coal samples. The estimates based on the laws of the statistical physics allow to obtain the computational expression for determination of the specific volume of the closed pores

$$\mu = \frac{P_0 - P}{Pm} V \quad (8)$$

where  $V$  is the volume of free spaces of the sorption ampule,  $m$  — is the mass of the sample,  $P_0$ ,  $P$  — initial and final pressures.

The time of establishing of the sorptional balance for high-porous solid substances is determined with the aid of the following expression [12]

$$\tau_2 = \mu R^2 / (v D_S), \quad (9)$$

where  $R$  is the size of solid particle. The structure of coal substance determines the scale for these time values as it is the structure that defines the coefficient  $D_S$  and the specific volume of gas molecules in the solid solution  $v$ .

**Conclusions.** Thus, as result of our investigations we found:

1. The organic coal substance in its natural state untouched by mine working at high geostatic pressures presents a solid solution. Physical and physico-chemical coal properties of coal and of gas-coal solid solutions are different.
2. Solid gas-coal solutions are metastable and degrade at variation of pressures and temperatures, which is accompanied by release of the gaseous phase.
3. A possibility of formation of secondary solid solutions with excessive methane or carbon dioxide concentrations at the regions of base rock pressure.
4. The amount of gas in the coal seam is defined by the free volume of pores and the amount of gas, diluted in coal substance.
5. Diluted gases in coals are the cause of microstresses at interfaces of different discontinuities, which in their turn can initiate new discontinuities, which makes the process of coal destruction a self-sustained one.
6. Methane sorbed on coals after the outburst, is weakly coupled in comparison with methane, sorbed on hazardous coals before the outburst. This is associated with decrease of number of free radicals in the coal structure.
7. Free gases are contained mainly in closed pores. The volume of them in most cases considerably exceeds the volume of open pores.

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