

THE ROLE OF OPEN AND CLOSED POROSITY IN THE KINETICS OF METHANE ABSORPTION (RELEASE) BY COALS

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The model of a solid containing open (connected with the external surface by channels) and closed pores is applied to a coal substance absorbing (or releasing) methane. The influence of the layer of adsorbed gas molecules on the kinetics of gas absorption (release) by a porous solid is investigated. It is established that the presence of closed porosity results in an increase of the gas release duration. The developed system of open pores promotes a decrease of the released gas quantity, i.e., it is followed by the gas release suppression.

Introduction

Being immediately concerned in the coal stratum gas-bearing capability, the problem of coal porosity and sorption phenomena connected with it is of great practical importance. The methane extraction during the coal mining is an essential addition to other power sources and all the investigations in this field are recognized to be very important for the NAS of Ukraine. In addition, the theoretical description of the methane release from coal may be spread to a wider spectrum of phenomena conditioned by the gas molecule diffusion in a porous solid (e.g., helium accumulation in the pores of construction materials in a reactor active zone). It becomes also possible to judge such values as the bond energy of a gas molecule in a solid and the quantity of pores, their size from experimental data. Besides, some conclusions about different diffusion models with respect to their applicability to porous solids can be made [1, 2].

Relations and Equations

We shall consider further how the methane pressure changes in a closed volume containing the coal substance in the form of spherical coal fractions (Fig. 1). The volume of the vessel is V_a , the fraction radius is R and their total volume is V . The surface of the coal fraction is not smooth; it has cracks and pores penetrating the bulk like channels, i.e., so-called open porosity is present (Fig. 2). In addition, the fractions contain closed pores (i.e., pores not connected with the external surface by channels). Their average radius \bar{r}_n is much less than the average distance l between

them which is also much less than the sphere radius R . Methane is distributed in pores, the free volume, and the coal substance where it is placed both in the solid solution and in the layer of adsorbed gas molecules on the inner surface of pores and on the external fraction surface. If the distribution is not equilibrium, the gas molecule exchange process takes place till the thermodynamic equilibrium is established. Thus, the gas pressure $P(t)$ in the free volume will change as well as the methane concentration in the coal substance.

The gas density in pores may be described with the rough characteristic $\rho(r, t)$, where r is the distance between a pore and the center of a sphere. The possibility of the roughage is connected with the implied small pore radius. The bulk concentration of the gas in the solid solution is described with the value $c(r, t)$. The mass transfer will be rendered by the diffusion equation:

$$\frac{\partial c(r, t)}{\partial t} = D \left(\frac{\partial^2 c(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial c(r, t)}{\partial r} \right) + Q(r, t), \quad (1)$$

where $Q(r, t)$ is the capacity of gas sources (or drains). We indicate the methane pressure at the initial moment of the process as P_0 and the solid solution concentration as c_0 :

$$P(0) = P_0, \quad c(r, 0) = c_0. \quad (2)$$

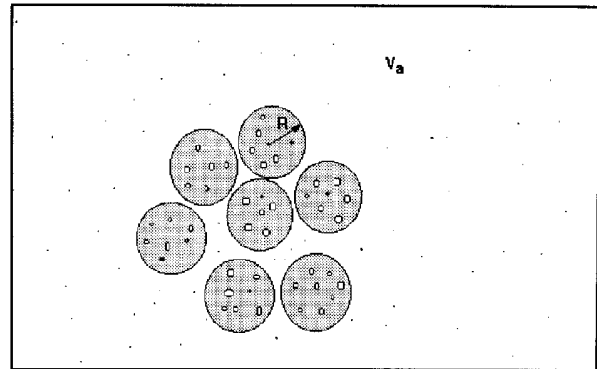


Fig. 1. Coal substance placed in the closed volume

Now we consider the boundary condition attached to Eq. (1). The methane arrival to the free volume from the coal substance is going not immediately but through the layer of gas molecules fallen out on the external surface of the coal fraction. The same situation takes place in pores. Thus, the boundary conditions should be formulated for two boundaries to solve a diffusion problem. The first boundary separates the methane solid solution in coal and the absorption layer. The second boundary parts the absorption layer and gas in a pore (or in the free volume). In the general case, these conditions are written as the proportion of the flux to the jump of the chemical potential while crossing the interface. As for the physical content, the coefficient of the proportion is the diffusion permeability of the boundary. The permeability is inversely proportional to the characteristic time of incorporation of a methane molecule into the boundary. More often, the time of incorporation is much less than the time of approaching the interface. Thus, the general boundary condition may be replaced with the equality of chemical potentials on both the sides of the interface. In other words, in the absorption layer, the chemical potential of methane is supposed to be equal to the chemical potential of the solid solution in the layer immediately adjacent to the absorption one. It does not mean that the chemical potential is constant for the whole coal volume. Due to a change of the chemical potential near the surface, the corresponding gradient of the chemical potential appears, which is followed by the flux of methane toward the surface (or from it). As for the interface between the absorption layer and ideal gas, the same boundary condition results in the proportion of the gas pressure to the gas molecule concentration in the absorption layer. The totality of these boundary conditions is equivalent to the Henry law, i.e., the gas pressure (and its density) is proportional to the gas concentration in a pore and on its surface:

$$c(r, t) = \nu \rho(r, t); \quad c_s(r, t) = \lambda \nu_s \rho(r, t) \quad (3)$$

and, correspondingly, $c_s(r, t) = \frac{\lambda \nu_s}{\nu} c(r, t)$. Here, ν is the solubility, ν_s is the surface solubility; λ is the distance between the neighbour sites on the surface which a methane molecule can occupy. It was mentioned in [3] that, according to the standard methods of statistical physics [4], the methane solubility in a solid is defined as

$$\nu = \frac{1}{\Omega} \left(\frac{2\pi h^2}{mT} \right)^{3/2} \left(\frac{T_r}{T} \right)^{3/2} \exp\left(-\frac{|\psi|}{T} \right), \quad (4)$$

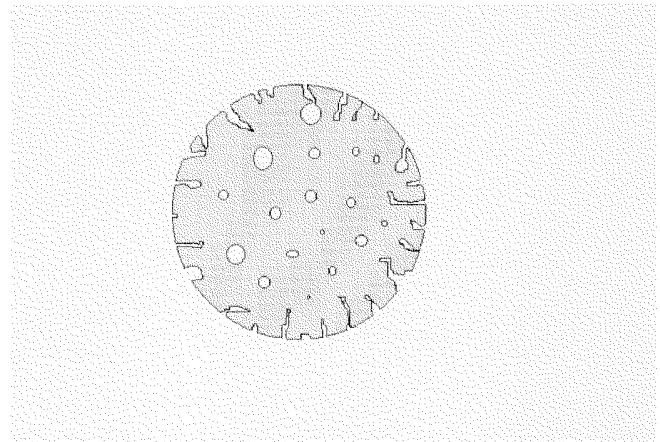


Fig. 2 Scheme of a coal substance fraction with closed and open pores

where $T_r = \left(\frac{18}{\pi} \right)^{1/3} \frac{h^2}{J}$ is the 'rotation temperature', m is the mass of a methane molecule, J is its inertia moment, $|\psi|$ is the energy of a methane molecule bond with the coal substance in the solid solution, Ω is the volume accounted for one site in the solid where the methane molecule can be built in ($\Omega \approx \lambda^3$). The experimental data [5, 6] allow the solubility to be estimated as $\nu \approx 10^{-2} - 1$. The surface solubility differs from the bulk one just at the point that the bond energy of a methane molecule in the bulk ψ is replaced with the bond energy on the surface χ . Usually, this energy is as great as a sufficient part of ψ (40 – 80%) with the same sign.

As a consequence of the instant equalization of the chemical potentials,

$$c(R, t) = \nu n(t) \quad \text{and} \quad c_s(R, t) = \lambda \nu_s n(t), \quad (5)$$

where $n(t)$ is the gas density in the free volume, $n(t) = \frac{N(t)}{V_c} = \frac{P(t)}{T}$.

In a porous solid, pores are the sources (or drains) of the gas arrival to the solid. The expression for the source capacity follows from the material balance condition. The change of the total number of molecules placed inside a pore in the form of ideal gas is equal to the sum of changes of the numbers of molecules absorbed on the pore surface and contained in the solid solution. Taking into account the Henry law, we have

$$Q(r, t) = -\frac{\gamma}{\nu} \left(1 + \frac{3\lambda \nu_s}{r_n} \right) \frac{\partial c(r, t)}{\partial t}, \quad (6)$$

where γ is the porosity of material, i.e., the total volume of pores divided by the total volume of material.

Eq. (1) may be rewritten in the form of the standard diffusion equation

$$\frac{\partial c(r, t)}{\partial t} = D_{\text{eff}} \left[\frac{\partial^2 c(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial c(r, t)}{\partial r} \right] \quad (7)$$

with the effective diffusion coefficient

$$D_{\text{eff}} = D \left(1 + \frac{\gamma}{v} \left(1 + \frac{3\lambda v_s}{r_n} \right) \right). \quad (8)$$

The condition of conservation of the total number of methane molecules looks as follows:

$$\frac{dN(t)}{dt} - \int \mathbf{J}(\mathbf{r}, t) d\mathbf{S} + \frac{d}{dt} \int c_s(\mathbf{r}, t) dS = 0, \quad (9)$$

where $d\mathbf{S}$ is a directed surface element. The integration is performed over the external coal fraction surfaces indented by open pores, and the normal vector is directed outside the fraction. The fluxes are presumed to be aligned with the sphere radius, and open pores are inferred not to penetrate the coal fraction too deeply. Then we obtain

$$\begin{aligned} & \left. \frac{V_c}{T} \frac{dP}{dt} + D \frac{\partial c(r, t)}{\partial r} \right|_{r=R} N_p 4\pi R^2 + \\ & + \frac{d}{dt} \left(\lambda v_s \frac{P(t)}{T} S_{\text{op}} \right) = 0, \end{aligned} \quad (10)$$

where S_{op} is the total surface area of the coal fractions with the open porosity taken into account without fail; N_p is the number of coal fractions. After the transition to the dimensionless variables $\tau \equiv \frac{t D_{\text{eff}}}{R^2}$ and $z \equiv \frac{r}{R}$, we obtain the relationship

$$\left. \frac{\partial c(z, \tau)}{\partial z} \right|_{z=1} = - \frac{(V_c + \lambda v_s S_{\text{op}})}{3VT \left[1 + \frac{\gamma}{v} \left(1 + \frac{3\lambda v_s}{r_n} \right) \right]} \frac{dP(\tau)}{d\tau} \quad (11)$$

or, introducing the designation $g \equiv \frac{V_c + \lambda v_s S_{\text{op}}}{3V [v + \gamma (1 + 3\lambda v_s / r_n)]}$,

$$\left. \frac{\partial c(z, \tau)}{\partial z} \right|_{z=1} = - g \frac{dP(\tau)}{d\tau}. \quad (12)$$

The parameter g is the main dimensionless parameter of the problem because it determines

sufficiently the kinetics of gas absorption into a porous solid. It is easily seen that, to within a factor 1/3, this parameter is equal to the ratio of the number of molecules in the free volume and on the external surface of the solid in equilibrium to their number in the solid (the sum over the solid solution, pores, and inner pore surfaces).

Eq. (7) with the initial (2) and boundary (5) conditions present the basic set applied to the analysis of the time-dependence of pressure in the free volume. Using the Laplace transformation of $P(z, \tau)$ and $c(z, \tau)$ with respect to time, we may write the result in the following form:

$$\begin{aligned} P(\tau) = & P_0 - \frac{1}{3g+1} \left(P_0 - \frac{c_0 T}{v} \right) + \\ & + 2g \left(P_0 - \frac{c_0 T}{v} \right) \sum_{k=1}^{\infty} \frac{\exp[-\pi^2 (k + \beta_k)^2 \tau]}{\pi^2 g^2 (k + \beta_k)^2 + 3g + 1}, \end{aligned} \quad (13)$$

where $0 < \beta_k < 1/2$, $\lim_{k \rightarrow \infty} \beta_k = 0$.

Discussion

If we compare (13) with the similar result obtained in [3], we can see that the consideration of open porosity results in the different dependence of g on external parameters. The total area of open pores and the surface solubility should be added to them. It should be also recalled that, according to (8), the methane absorption on closed pores decreases the effective diffusion coefficient. So the gas release time increases. The asymptotic dependences $P(t)$ remain valid. In particular, if the time value is large, $\tau \gg 1/\pi^2$, the pressure approaches the equilibrium in accordance with the exponential law:

$$P(\tau) \approx P_{\infty} + 2g \left(P_0 - \frac{c_0 T}{v} \right) \frac{\exp[-\pi^2 (1 + \beta_1)^2 \tau]}{\pi^2 g^2 (1 + \beta_1)^2 + 3g + 1}, \quad (14)$$

where

$$P_{\infty} = P_0 - \frac{1}{3g+1} \left(P_0 - \frac{c_0 T}{v} \right). \quad (15)$$

If we consider now the small time case, $\tau \ll 1/\pi^2$, we can see that, in the case $g \gg 1$, the gas pressure asymptote looks like the 'square-root-law' which is characteristic of diffusion processes:

$$P(\tau) \approx P_0 - \frac{2}{\pi g} \left(P_0 - \frac{c_0 T}{v} \right) \sqrt{\tau}. \quad (16)$$

The same relationship holds true for $g \ll 1$ if the time is extremely small, $\tau \ll g^2 \ll 1/\pi^2$. In the intermediate time area, $g^2 \ll \tau \ll 1/\pi^2$, the calculation gives the 'inverse-square-root-law'

$$P(\tau) \approx P_\infty + \frac{2g}{\pi\sqrt{\tau}} \left(P_0 - \frac{c_0 T}{v} \right). \quad (17)$$

Thus, two or three stages of the pressure change take place as before (under $g \gg 1$ or $g \ll 1$, correspondingly). But this parameter is determined by the values of the open and closed porosity as well as by the surface and bulk solubility.

The definition of g may be rewritten as follows:

$$g = \frac{1}{3} \left[\frac{V_c}{V} + \frac{\lambda S_{op}}{V} v_s \right] \left[v + \gamma + \frac{\lambda S_{cl}}{V} v_s \right]^{-1}, \quad (18)$$

where $\frac{S_{op}}{V}$ (and $\frac{S_{cl}}{V}$) is the total area of open and closed pores in the bulk, correspondingly. It is explicitly seen that the presence of the developed surface of open pores can enhance g vastly. While speaking about a 'developed surface', we keep in mind some effective volume $\sim \lambda S_{op}$ (or λS_{cl}). This is the volume of the layer adjacent to the pore surface where methane molecules can be incorporated. In the terms of the fractal theory, it means that λ is the scale for length measurements. In addition, an increase of g means the suppression of the gas release because a pressure change in the free volume is inversely proportional to this parameter:

$$\Delta P \equiv P_0 - P_\infty = \frac{1}{3g+1} \left(P_0 - \frac{c_0 T}{v} \right). \quad (19)$$

Fig. 3 shows how the value of g influences a gas pressure change in the free volume. The calculation shows that, under real values of the bulk and surface solubilities, the dominating open porosity (the ratio

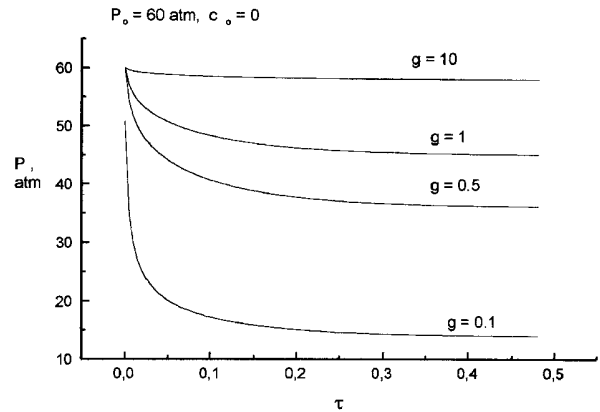


Fig. 3. Methane pressure change in the closed volume around the coal substance ($P_0 = 60 \text{ atm}$, $c_0 = 0$)

$S_{op} / S_{cl} \sim 10$) enlarges g three-fold in comparison with the result obtained in [3]. It makes the pressure change ΔP to decrease by half. Thus, the gas release suppression effect appears to be rather distinct.

The presence of the layer of adsorbed gas molecules on the surface of closed pores is responsible for a decrease of the effective diffusion coefficient. In addition, it tends to decrease g to some extent.

Conclusions

Being taken into account in such a manner, adsorption is associated with two main effects. First, it results in a decrease of the effective diffusion coefficient because of the closed porosity influence. Hence, the duration of the process grows. Second, the dominating open porosity enlarges the g parameter and the closed porosity lowers it. This affects the quantity of the gas released (absorbed) by the coal substance. In other words, the inclusion of the gas molecule adsorption processes on the open and closed pore surfaces allows to estimate the gas-bearing capacity of coal more accurately.