
The coal-gas system – the effective diffusion coefficient

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Abstract: In this paper issues concerning the evaluation of the kinetics of gas release from coal samples were systematised. Our own analytical solution was presented. Diffusion equation was solved numerically. The numerical solution of Fick's formula taking into account of the Langmuir isotherm was compared with the analytical solution based on the Henry isotherm. For the initial range of pressure values, where Langmuir and Henry isotherms were similar, the differences were relatively minor. However, they become significant for the higher pressure values. [Received: January 8, 2015; Accepted: March 4, 2015]

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1 Introduction

Traditionally, the physicochemical processes whose result is the release of gas from a coal sample – often referred to as desorption – are discussed in relation to three phenomena: the desorption proper of gas from the coal's pore surface, the diffusion of gas within grains, and the filtration of gas through the system of fissures and large pores (Harpalani and Chen, 1997; Pillalamarry et al., 2011; Gawor and Skoczylas, 2014). The release of gas from coal is caused by a reduction of the pressure (and, indirectly, of the density) of the gas surrounding the rock. Under in situ conditions, such a situation is inextricably linked to mining activities. When headings are drilled, or when a longwall is

exploited, the original pore pressure of gas in a rock mass is reduced as a result of the release of gas from the unmined coal into a heading through cracks in the former. Observation of the temporal course of the release of methane from a coal sample makes it possible to analyse the diffusion processes accompanied by desorption of the originally bonded gas. If we take into account the fact that the desorption proper occurs almost instantaneously, and the filtrational flow of gas among the sorbent grains is fast when compared to the diffusion process occurring inside the grains, we shall see that the decisive factor influencing the kinetics of gas release is nothing else but diffusion. The basic parameter describing the combined processes of sorption and diffusion is the so-called effective diffusion coefficient, mentioned by Timofejew (1967) and defined as:

$$D = \frac{D_e \frac{\varepsilon}{k^2}}{1 + \Gamma} \quad (1)$$

In comparison with the physical diffusion coefficient, the effective diffusion coefficient involves additional factors determining the sorption isotherm and porosity. The effective diffusion coefficient is laboratory-determined, and the process is based on the registration of the kinetics of gas release from a granular coal sample.

In the global mining sector, the effective diffusion coefficient, understood as a parameter of the coal-gas system, is seldom used for industry-related purposes. This is due to a number of factors, among which the most important ones are the practical problems connected with determining this parameter. To do this, it is often necessary to apply some complex and costly equipment (such as sorption gravimetric devices). It should be noted that the potential beneficiaries of the research results (i.e., colliery management and staff) might not have sufficient experience that would let them interpret these results properly.

At the same time, the benefits resulting from the application of this parameter are huge (Wierzbicki, 2011). The value of the effective diffusion coefficient D_e of methane in coal varies naturally in the range $5 \cdot 10^{-7} \div 10^{-11} \left[\frac{cm^2}{s} \right]$. Such high variability of the D_e

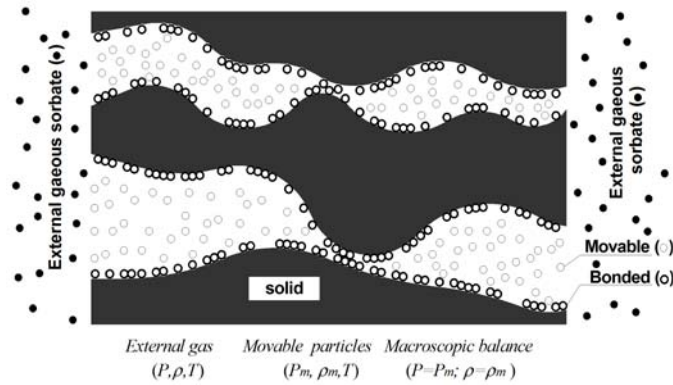
value implies serious consequences – the mining circumstances (viewed from the perspective of the analysis of the methane hazard, as well as gas and rock outburst hazard) are considerably different when we deal with coals that have similar methane content, but significantly disparate diffusion coefficients. For instance, a coal characterised by a higher value of the diffusion coefficient (Skoczylas, 2012a) (for the same grain-size distribution observed in the comminuted coal mass) is going to release into excavations the same amount of gas, but in an accordingly shorter period of time. For researchers, a high value of the diffusion coefficient is often a signal that the investigated coal has a peculiar structure, most often resulting from the proximity of geological deformations. Needless to say, this constitutes a considerable danger as far as the outburst threat is concerned (Wierzbicki and Dutka, 2010; Młynarczuk and Wierzbicki, 2009; Clarkson and Bustin, 1999a, 1999b; Skoczylas and Wierzbicki, 2014; Li et al., 2003; Wierzbicki and Skoczylas, 2014).

The Authors of the present paper believe that our knowledge concerning the evaluation of the kinetics of gas release from coal samples should be systematised. Similarly, it is advisable to identify the numerous aspects which significantly influence the evaluation of the effective diffusion coefficient, yielding potential inaccuracies.

2 The processes occurring inside a coal grain

Let us consider now a grain of a porous sorbent, surrounded with a gaseous sorbate. Let us assume that the sorbent pores form a network, due to which transportation of particles within the grain is possible. The interdependent processes of intercepting and transporting sorbent that occur within the grain shall be treated as isothermal ones.

Figure 1 Macroscopic balance



In such processes, the external gaseous sorbate and the sorbate accumulated in the network of sorbent pores take part. The accumulated sorbate is twofold in nature (Figure 1). The bonded sorbate consists of particles that are stuck in the pore walls and thus not able to migrate. The movable sorbate consists of particles which can migrate along the network of pores. Due to thermal impulses, the two types of the sorbate can exchange their particles. In the state of equilibrium, this exchange is balanced. The partial density ρ_m of the movable sorbate is the mass of the movable sorbate included in the pore unit volume. The mass of the movable sorbate included in the sorbent unit volume is the partial concentration c_m of the movable sorbate. Analogously, the partial density ρ_b and the partial concentration c_b of the bonded sorbate are defined. Under isothermal conditions, these parameters determine the state of the fraction of the accumulated sorbate. The densities and concentrations are interconnected by the value of the sorbent porosity ε , and can be applied interchangeably:

$$c_m [\text{mol}/\text{m}^3] = \rho_m \varepsilon \quad \text{and} \quad c_b = \rho_b \varepsilon \quad (2)$$

Partial densities and concentrations can be treated as local quantities, which are usually dependent on the sorbate location within the sorbent.

2.1 The sorption isotherm

The sorption equilibrium is usually defined as the macroscopic balance between a sorbent grain and a gaseous sorbate surrounding it, at constant temperature and density (pressure) of the external gas. After the sorbent grain has been saturated for a sufficient period of time, the exchange of sorbate between the grain and the outer environment ceases. The exchange between both fractions of the sorbate accumulated within the grain stops as well. The macroscopic sorption equilibrium, thus understood, is described by means of

sorption isotherms. An isotherm shall be viewed as a relationship between the concentration of the bonded sorbate and the saturation conditions. In the light of this definition, the formula for a sorption isotherm is as follows:

$$c_b = F(\rho) = \varepsilon \rho_b; \frac{\partial \rho_b}{\partial t} = \frac{\partial \rho_m}{\partial t} = \frac{\partial T}{\partial t} = 0, \quad (3)$$

2.2 The macroscopic and local sorption equilibriums

The equilibrium described by means of the isotherm (3) is macroscopic in its nature. The equilibrium concerns both the inside and the outside of the grain. Fractions of the sorbate accumulated within the grain remain in the state of mutual equilibrium. Within the grain, local values of the partial concentrations and densities of these fractions are constant.

As is the case with the particles of classic gases, the particles of a movable sorbate can also be discussed in relation to pressure. The Author hereby assumes that this pressure – again, just as with classic gases – is determined by the partial density ρ_m and the temperature of the movable sorbate at the same time. When the temperature is constant, the gas pressure is directly proportional to the gas density. The Author assumes that an analogous dependence can be ascribed to a movable sorbate. Taking into consideration the potential different properties of these media, we assume that the density ρ of a classic gas and the density ρ_m of a movable sorbate are proportional, under the same conditions:

$$\rho = \alpha \rho_m \quad (4)$$

The density ρ_m of a movable sorbate usually depends on time and localisation. In areas where there is ‘communication’ between the sorbent pore system and the external environment, the pressure of the external gas and the pressure of the movable sorbate are equal. This means that, as stated in equations (3) and (4), the density ρ of an external gas is determined by the density ρ_m (or concentration) of a movable sorbate and the density (or concentration) of the bonded sorbate:

$$\rho_b = \frac{1}{\varepsilon} F(\alpha \rho_m) c_b = F(\alpha \rho_m). \quad (5)$$

Under the conditions of the macroscopic sorption equilibrium, the same can be said about any other location within the pore system. The condition (4) may also be viewed as a local condition, if the macroscopic sorption equilibrium does not hold.

2.3 Processes occurring with the local sorption equilibrium preserved

Any location for which the condition (5) is fulfilled is referred to as a location in the state of the local sorption equilibrium. In such location, there is local equilibrium between the two fractions of the accumulated sorbate (also in a situation when, due to a non-stationary process occurring within the sorbent, the partial concentrations of sorbates depend both on location and time).

The process occurs with the state of the local sorption equilibrium preserved only if the condition (5) is fulfilled for the whole zone where this process is happening, and for every second of the process duration. Preserving the local sorption equilibrium is

conditioned by a sufficient rate of exchange between the sorbate fractions. Due to this exchange, the equilibrium of both fractions, distorted by the ongoing processes, is equalised.

2.4 *The equation describing the processes of release (accumulation) of a gaseous sorbate under the conditions of the local sorption equilibrium preserved*

It has been assumed that the transportation of a sorbate within a sorbent is, in fact, the diffusion of the movable sorbate particles, propelled by the gradient of the partial concentration of the sorbate. If our considerations are limited to a one-dimensional case, then, according to Fick's first law, the density J of the stream of diffusing movable sorbate particles can be described by means of the diffusion coefficient D :

$$J = -D \frac{\partial c_m}{\partial x} \quad (6)$$

The diffusion of the movable sorbate evokes changes in the total concentration $c_m + c_b$ of the accumulated sorbate. These changes can be described by means of Fick's second law:

$$\frac{\partial (c_m + c_b)}{\partial t} = D \nabla^2 c_m \quad (7)$$

If the condition concerning the existence of the local equilibrium (5) is fulfilled, the local total concentration of the sorbate is:

$$c_m + c_b = c_m + F(\alpha \rho_m); \quad (8)$$

Taking equations (7) and (8) into consideration, we arrive at the following formula describing the changes in the concentration of the movable sorbate (for one-dimensional case):

$$\frac{\partial (c_m + c_b)}{\partial t} = \frac{\partial c_m}{\partial t} \left(1 + \frac{\alpha}{\varepsilon} \frac{\partial F(\rho)}{\partial \rho} \right) = \frac{\partial^2 c_m}{\partial x^2} \quad (9)$$

For the three-dimensional case, the formula (9) is as follows:

$$\frac{\partial c_m}{\partial t} = D \nabla^2 c_m, \quad \text{where} \quad D_e = D \left(1 + \frac{\alpha}{\rho} \frac{\partial F(\rho)}{\partial \rho} \right)^{-1} \quad (10)$$

2.5 *The effective diffusion coefficient*

Assuming that Henry's linear formula can be adopted as the isotherm:

$$c_b = F(\rho) = H\rho, \quad (11)$$

the parameter D_e in the formula (10) assumes a value that is constant:

$$D_e = D \left(1 + \frac{\alpha}{\varepsilon} H \right)^{-1}. \quad (12)$$

The value in question is identical with the effective diffusion coefficient as described in (Timofejew, 1967). Thus, the formula (10) assumes the form of Fick's second law. An analytical solution to such an equation, for a unipore model, is provided by Crank (1956). The solution describes the changes in the mass $M(t)$ of the sorbate that is entering or leaving the sorbent grain during the transition from one state of macroscopic sorption equilibrium to another:

$$\frac{M(t)}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n}\right)^2 \exp\left(-\frac{D_e n^2 \pi^2 t}{R^2}\right) \quad (13)$$

With the unipore model of diffusion, the following assumptions are made:

- the process is of isothermic nature
- the gas is released from a spherical grain with radius R
- until the initial moment $t < 0$, the grain is evenly saturated with gas
- in the $t = 0$ moment, an abrupt change of the concentration of the gas surrounding the grain occurs, which sets in motion the processes of sorbate desorption and transportation
- the gas release kinetics depends solely upon the kinetics of the diffusional transportation of gas particles within the grain.

If we assume that a granular coal sample is an equivalent of a bed of spherical grains, then – fitting the parameters of the formula (13) to the registered course of the changes in the sorbate mass $M(t)$ during the transition from one state of macroscopic sorption equilibrium to another – we are able to determine the effective diffusion coefficient for the sorbate-sorbent system. Timofeev provides us with a simplified form of this procedure. Once we solve the equation (13), searching for the moment $t_{1/2}$ for which the mass of gas equals 50% of the initial mass:

$$\frac{M(t)}{M_\infty} = \frac{1}{2} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n}\right)^2 \exp\left(-\frac{D_e n^2 \pi^2 t}{R^2}\right), \quad (14)$$

we will obtain Timofeev's formula:

$$D_e = \frac{0.308 \cdot R^2}{\pi^2 \cdot t_{1/2}} \quad (15)$$

It needs to be emphasised, however, that the effective diffusion coefficient is a parameter related to engineering, and – as such – can be used in the process of evaluating the probability of occurrence of methane hazards, as well as of gas and coal outbursts (among other things). In a purely physical sense, it is difficult to secure required boundary conditions and linearities of sorption isotherms for the sake of an experiment. In such a situation, the numerical solution to the equation (8) seems to be much more proper.

If we want to use Crank's analytical solution, we need to take into account the fact that the value of the determined effective diffusion coefficient is additionally influenced by (among others):

- the sorption isotherm
- the initial and final sorbate pressure in the conducted experiment
- the rate of changes in the pressure value during the experiment.

It is therefore necessary to supplement the results of the research into the diffusivity of the sorbate-sorbent system with the information regarding the conditions in which the experiment was conducted. Comparing the values of the effective diffusion coefficient established with various equipment and with various measurement methods may prove troublesome.

2.6 *The diffusion coefficient and the sorption isotherm*

The assumption regarding the linear nature of the sorption isotherm made it possible to obtain an analytical solution to the diffusion formula (10). However, making this assumption results in significant discrepancies between the numerical (Langmuir's) solution, which takes into account the real sorption isotherm, and the analytical solution based on the linear (Henry's) isotherm. In currently exploited coal beds, the value of the seam pressure of methane is usually between less than ten and ten-odd bar (Skoczylas, 2012b). Thus, the application of the model based on a simplified linear isotherm becomes much more difficult.

In order to illustrate the discussed problem, the temporal courses of the emissions of sorbate from the porous sorbent were generated. The numerical solution to the formula (10) takes into account a Langmuir's isotherm (solid line, Figure 2) that is typical for the sorption of methane on hard coal. The isotherm's parameters are $s(P) = \frac{s_{\max} \cdot b \cdot P}{1 + b \cdot P}$,

$$s_{\max} = 20 \left[\frac{\text{cm}^3 \text{CH}_4}{\text{g}} \right], \quad b = 0.2 \left[\frac{1}{\text{bar}} \right].$$

Also, Henry's isotherms for the sorption points were determined on the basis of Langmuir's isotherm: 0-1 bar, 0-3 bar, 0-6 bar, 0-12 bar, 0-18 bar (dotted lines, Figure 2.). Subsequently, the temporal courses of the release of methane from a sample coal grain fraction were generated, for a typical value of the diffusion coefficient. In the charts 3-7, the solid line represents the release of methane from a coal sample as shown with Langmuire's isotherm [the numerical solution to the formula (10)], and the dotted line represents the emission as shown with Henry's linear isotherms [the analytical solution (13)]. According to expectations, for the initial range of pressure values (Figure 3), where Langmuir's and Henry's isotherms are similar, the differences are relatively minor. However, they become significant for higher pressure values (Figures 5-7).

Figure 2 Langmuir isotherm and Henry isotherms

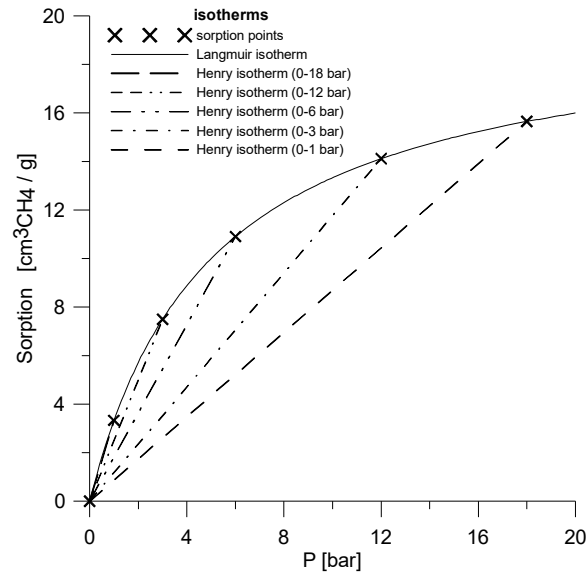


Figure 3 Diffusions models with Henry and Langmuir isotherms (P1 = 1 [bar], P2 = 0 [bar])

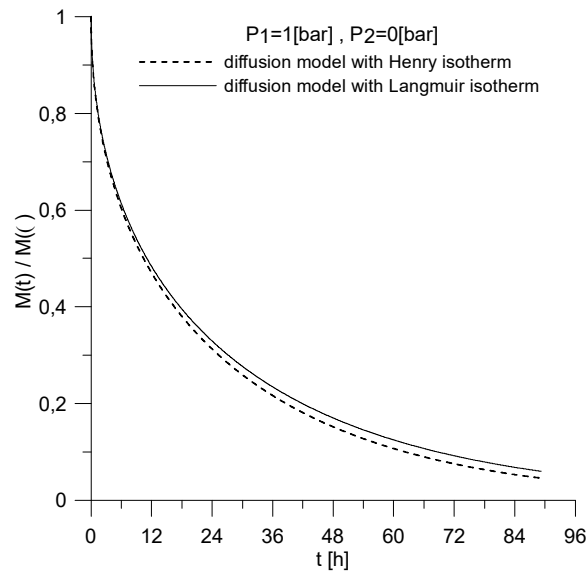


Figure 4 Diffusions models with Henry and Langmuir isotherms ($P_1 = 3$ [bar], $P_2 = 0$ [bar])

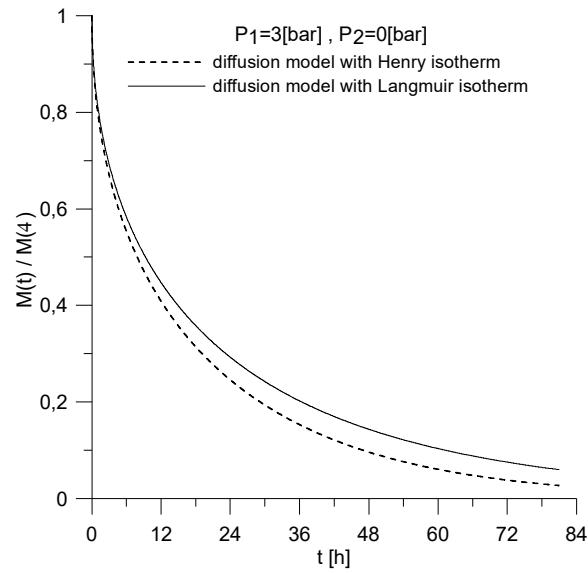


Figure 5 Diffusions models with Henry and Langmuir isotherms ($P_1 = 6$ [bar], $P_2 = 0$ [bar])

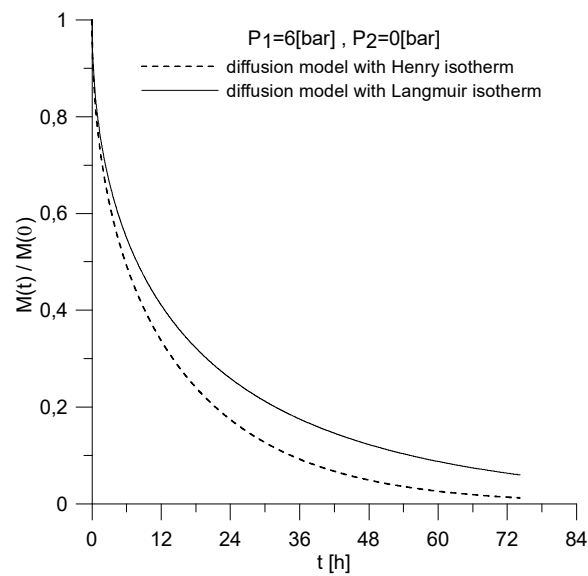


Figure 6 Diffusions models with Henry and Langmuir isotherms ($P_1 = 12$ [bar], $P_2 = 0$ [bar])

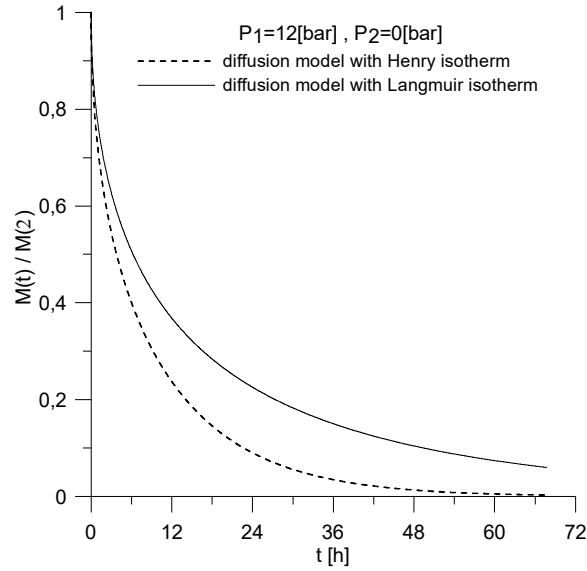
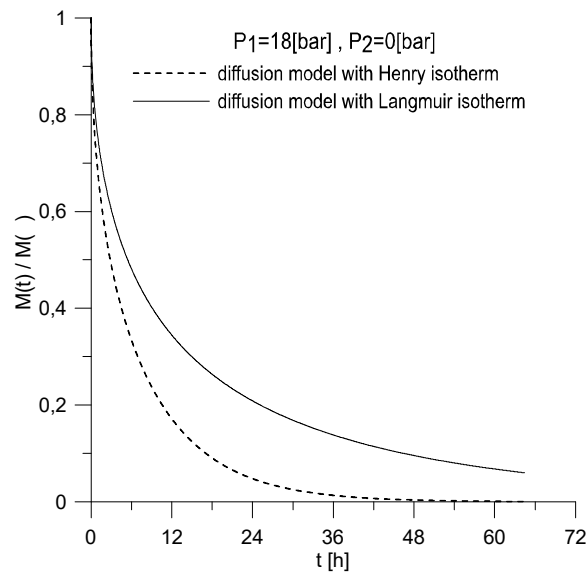


Figure 7 Diffusions models with Henry and Langmuir isotherms ($P_1 = 18$ [bar], $P_2 = 0$ [bar])

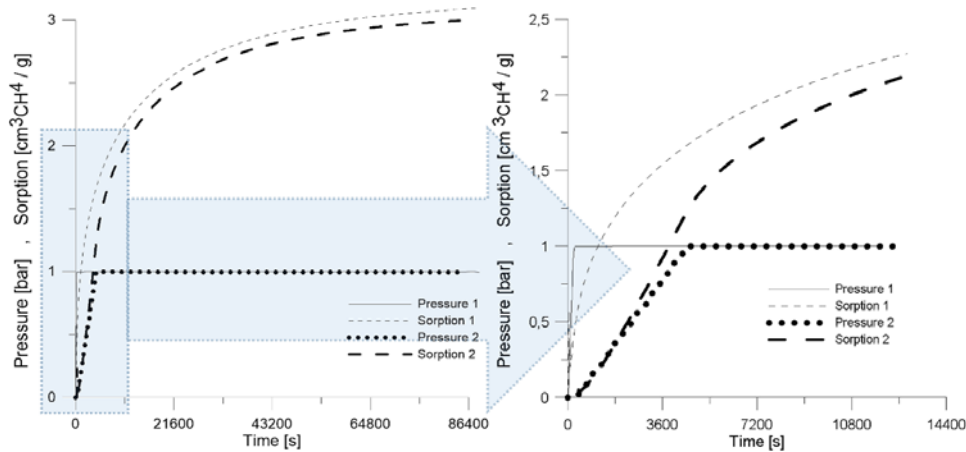


2.7 The diffusion coefficient in relation to other vital parameters

Temperature influences the value of the diffusion coefficient in a significant way (Baran et al., 2014a, 2014b). Research shows that the higher the temperature during an experiment, the higher the value of the coefficient in question. This is supported by intuitive knowledge, as thermal vibrations of gas molecules are a factor that determines the course of the diffusion process. Wierzbicki (2013) observed a double increase in the value of the diffusion coefficient, with a rise in the temperature value from 290 [K] to 330 [K].

One of the key assumptions of the unipore model – on the basis of which the diffusion coefficient is determined – concerns a step change in the pressure (concentration), viewed as the initial condition of the performed observation. If we assume that the sorbate release/accumulation lasts several ours, we should expect that the process is the most dynamic during the initial several dozen minutes. If the technical aspects of a given experiment exclude a step change in the pressure value (as is the case with IGA-type gravimetric analysers), the discussed aspect influences significantly the determined value of the diffusion coefficient. In order to present the problem in a more comprehensive way, the Author carried out two experiments using the same coal material. Before the experiments actually took place, coal samples were subjected to total outgassing in a vacuum, for 24 hours. In the first case, the quasi-step change in the pressure value lasted ca. 240 seconds; in the second one – ca. 3,600 seconds (cf. Figure 8). Just as it was expected, in the first case, the diffusion (thin dotted line) occurred faster than in the second case (thick dotted line). This resulted in relevant changes in the value of the diffusion coefficient – $1.04 \cdot 10^{-9}$ [cm²/s] for a fast pressure change and $0.66 \cdot 10^{-9}$ [cm²/s] for slow pressure change.

Figure 8 Methane emissions from coal - fast and slow pressure changes (see online version for colours)



The arguments presented here prove that the diffusion coefficient is a parameter that is highly sensitive to all the parameters involved in an experiment. In order to discuss the value of the diffusion coefficient, one has to adopt measurement procedures that would be possibly most compatible with the assumptions of the unipore model.

3 Summary

The accumulation of a sorbate in a sorbent, as well as the release of a sorbate from a sorbent, are phenomena of extreme significance when it comes to engineering and its numerous aspects. In order to properly evaluate the natural risks connected with the presence of gas in hard coal seams – in particular, of the methane hazard and the gas and rock outburst hazard – one has to know not only the exact amount of gas included in coal, but also the speed with which it is released. The parameter which describes the kinetic aspects of the emission of gas from a hard coal sample is known as the effective diffusion coefficient. However, its application poses certain problems, both metrological and interpretative. The analytical solution to the diffusion equation (13), among some other numerous boundary conditions, makes use of an assumption that the sorption isotherm is linear. During an actual experiment on a given research material, such as hard coal, both the boundary conditions and the linearity of the sorption isotherm cannot be secured. Depending on the measurement method, this results in discrepancies between the analytical solution and the numerical (i.e., the one that takes into account Langmuir's isotherm) solution to the diffusion equation. Thus, providing a precise description of the adopted measurement method and the chosen solution to the diffusion equation, used in the process of determining the effective diffusion coefficient, becomes absolutely essential.

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References

- Baran, P., Rogozińska, J., Zarębska, K. and Porada, St. (2014b) 'Analysis of the coal-gas system for intensification of methane recovery with carbon dioxide', *Chemical Review*, Vol. 93, No. 12, pp.2008–2012, DOI:10.12916/przemchem.2014.2008.
- Baran, P., Zarębska, K. and Nodzeński, A. (2014a) 'Energy aspects of CO₂ sorption in the context of sequestration in coal deposits', *Journal of Earth Science*, Vol. 25, No. 4, pp.719–726, DOI: 10.1007/s12583-014-0459-x.
- Clarkson, C.R. and Bustin, R.M. (1999a) 'The effect of pore structure and gas pressure upon the transport properties of coal: a laboratory and modeling study 1. Isotherms and pore volume distributions', *Fuel*, September, Vol. 78, No. 11, pp.1333–1344.
- Clarkson, C.R. and Bustin, R.M. (1999b) 'The effect of pore structure and gas pressure upon the transport properties of coal: a laboratory and modeling study 2. Adsorption rate modeling', *Fuel*, September, Vol. 78, No. 11, pp.1345–1362.
- Crank, J. (1956) *Mathematics of Diffusion*, Oxford University Press, London.
- Gawor, M. and Skoczylas, N. (2014) 'Sorption rate of carbon dioxide on coal', *Transport in Porous Media*, January, Vol. 101, No. 2, pp.269–279.
- Harpalani, S. and Chen, G. (1997) 'Influence of gas production induced volumetric strain on permeability of coal', *Geotech. Geol. Eng.*, December, Vol. 15, No. 4, pp.303–325.
- Li, H., Ogawa, Y. and Shimada, S. (2003) 'Mechanism of methane flow through sheared coals and its role on methane recovery', *Fuel*, July, Vol. 82, No. 10, pp.1271–1279.

- Młynarczuk, M. and Wierzbicki, M. (2009) 'Stereological and profilometry methods in detection of structural deformations in coal samples collected from the rock and outburst zone in the 'Zofiówka' Colliery', *Archives of Mining Sciences*, Vol. 54, No. 2, pp.189–201.
- Pillalamarry, M., Harpalani, S. and Liu, S. (2011) 'Gas diffusion behavior of coal and its impact on production from coalbed methane reservoirs', *International Journal of Coal Geology*, June, Vol. 86, No. 4, pp.342–348.
- Skoczylas, N. (2012a) 'Laboratory study of the phenomenon of methane and coal outburst', *International Journal of Rock Mechanics & Mining Sciences*, October, Vol. 55, pp.102–107 [online] <http://www.sciencedirect.com/science/article/pii/S1365160912001347>.
- Skoczylas, N. (2012b) 'Coal seam methane pressure as a parameter determining the level of the outburst risk – laboratory and in situ research', *Arch. Min. Scs.*, December, Vol. 59, No. 4.
- Skoczylas, N. and Wierzbicki, M. (2014) 'The outburst risk as a function of the methane capacity and firmness of a coal seam', *Arch. Min. Sc.*, Vol. 59, No. 4, pp.1023–1031.
- Timofejew, D. (1967) *Adsorptionkinetik*, Lipsk Veb.
- Wierzbicki, M. (2011) 'Effect of selected simplifications of the unipore model upon the result of the study of the diffusion coefficient in coal', *Archives of Mining Sciences*, Vol. 56, No. 4, pp.761–776.
- Wierzbicki, M. (2013) 'Changes in the sorption/diffusion kinetics of a coal-methane system caused by different temperatures and pressures', *Mineral Resources Management*, Vol. 29, No. 4, pp.155–168.
- Wierzbicki, M. and Dutka, B. (2010) 'The influence of temperature changes of the structurally deformed coal – methane system on the total methane content', *Arch. Min. Sci.*, Vol. 55, No. 3, pp.547–560.
- Wierzbicki, M. and Skoczylas, N. (2014) 'Evaluation and management of the gas and rock outburst hazard in the light of international legal regulations', *Arch. Min. Sc.*, Vol. 59, No. 4, pp.1119–1129.