

MARCIN KARBOWNIK^{1*}, JERZY KRAWCZYK²,
TOMASZ SCHLIETER³

THE UNIPORE AND BIDISPERSE DIFFUSION MODELS FOR METHANE IN HARD COAL SOLID STRUCTURES RELATED TO THE CONDITIONS IN THE UPPER SILESIA COAL BASIN

The safety of mining operations in hard coal mines must be constantly developed and improved. There is ongoing multi-directional research focused at best recognition of the phenomenon associated with the properties of the coal-gas system and its connections with mining and geological conditions. This article presents the results of sorption experiments on coals from the Upper Silesian Coal Basin, which are characterized by varying degrees of coalification. One of the parameters that describes the kinetics of methane sorption, determining and providing valuable information about gas hazard and in particular the risk of gas and rock outbursts, is the effective diffusion coefficient D_e . It is derived from the solution of Fick's second law using many simplifying assumptions. Among them is the assumption that the carbon matrix consists of only one type of pore – micropores. In fact, there are quite often at least two different mechanisms, which are connected to each other, related to the diffusion of methane from the microporous matrix and flows occurring in voids and macropores. This article presents both the unipore and bidisperse models and a set of comparisons which fit them to experimental curves for selected coals. For some samples the more complex bidisperse model gave much better results than the classic unipore one. The supremacy of the bidisperse model could be associated with the differences in the coal structure related to the coalification degree. Initial results justify further analyses on a wider set of coals using the methodology developed in this paper.

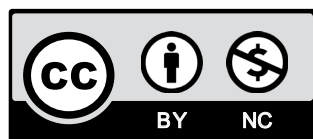
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¹ CENTRAL MINING INSTITUTE, 1 GWARKOW SQ., 40-166 KATOWICE, POLAND

² STRATA MECHANICS RESEARCH INSTITUTE POLISH ACADEMY OF SCIENCES, 27 REYMONTA STR., 30-059 KRAKOW, POLAND

³ SILESIA UNIVERSITY OF TECHNOLOGY, 2A AKADEMICKA STR., 44-100 GLIWICE, POLAND

* Corresponding author: mkarbownik@gig.eu



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1. Introduction

The analysis of phenomena related to gas transport in the coal structure is important in the context of preventing natural hazards, such as methane hazard and gas and rock outbursts. In hard coal mines increasing the level of safety during mining operations is a continuous process. There is ongoing research which is designed to identify the phenomena associated with the properties of the coal-gas system and their changes in relation to their mining and geological conditions. The level of saturation of the coal deposit with methane increases as does the seismic activity of the rock mass as the depth of mining works increases (Krause, 2005; Szlązak, 2013). Therefore, it is fundamental and desirable to increase the level of safety by conducting research aimed at understanding the phenomenon of sorption and gas transport in the carbon structure. Through studies of the kinetics of the accumulation and release of gas from the coal structure, valuable information is provided regarding porosity, the presence of gas in coal seams and the possibility of its rapid outflow which can initiate gas and rock outburst.

An analysis of the available publications indicates that there is a strong relationship between the degree of coalification and gas diffusion kinetics (Crosdale et al., 1998; Laxminarayana & Crosdale, 1999). Change in the porous structure is closely related to change in the degree of coalification. The pores differ in shape and size (Bukowska et al., 2012). It has been determined that the diffusivity of coal decreases with the increase in the degree of coalification due to the growth in the share of micropores in its structure (Bush et al., 2004). Based on the previous research it was found that achieving sorption equilibrium is faster in coals with a low degree of coalification than in the case of coals with a high degree of coalification, such as anthracite (Li et al., 2010).

The velocity of sorption processes in porous media can be estimated on the basis of data concerning sorption isotherms and gas diffusion models, which include the unipore and bidisperse diffusion models. The unipore model finds its application in the description of gas sorption in the case of structures in which only one type of pore occurs – micropores. The bidisperse model is used for structures with different pore size distribution, where diffusion occurs in parallel in both macropores and micropores. Therefore, experiments must include all occurring phenomena (Dang et al., 2017).

One of the key parameters that describes the kinetics of methane sorption, which determines and provides valuable information about the threat of gas and rock outbursts, is the effective diffusion coefficient D_e derived from the solution of Fick's second law (Hobler, 1976) obtained using many simplifying assumptions. One of these states that the carbon matrix consists of only one type of pore – micropores. In fact, there are quite often at least two different mechanisms that are connected to each other and are related to the diffusion of methane from the microporous matrix and flows occurring in voids and macropores (Keshavarz et al., 2017). Currently, in Poland, the unipore model is used to describe the kinetics of methane sorption in hard coal; the sorption/diffusion kinetics are described using the effective diffusion coefficient from Crank's mathematical solution (Crank, 1975).

Gas migration processes, sorption and desorption are also subject to modelling by numerical methods (Crosdale et al., 1998; Clarkson & Bustin, 1999; Pan et al., 2010; Dang et al., 2017; Li et al., 2019). The results of a simulation may significantly depend on the extent to which the model represents the real properties of the medium. Specifying the parameters of the bidisperse model will enable its use for numerical analyses. Comparison of the results for both descriptions of sorption kinetics will enable the assessment of to what extent the use of a more accurate description may affect the quality of numerical modelling.

This work presents attempts to adapt model runs using the unipore and bidisperse models to the actual course of the methane sorption process in hard coal obtained as a result of the experiments. In addition, the results and dependencies will be combined with changes in the degree of coalification resulting from the content of volatile matter in selected mines from the Upper Silesian Coal Basin. The content of volatile matter in hard coal, which is calculated by converting its value to a dry and ashless state, is the basic parameter used to classify types of coal. This relationship was determined in both the Polish standard PN-G-97002:2018-11, as well as the international classification UN-ECE 1988. The results of experiments will enable the determination of the conditions in which the unipore model is acceptable and when it becomes necessary to use a bidisperse model.

2. Materials and methods

2.1. Research Area

The Upper Silesian Coal Basin was designated as the research area in which four mines that are differentiated in terms of coal types and volatile matter content were selected. Samples were taken from the following coal mines: the Szczygłowice mine, Zofiówka mine, Brzeszcze mine and Sobieski mine. Based on the relationship between the degree of coalification and volatile matter content specified in the PN-G-97002:2018-11 standard, these mines were selected, and in these mines the volatile matter content is both above 30% and below 30%. This selection will enable a clear presentation of the validity of using one of the two models presented. Table 1 summarizes the results of determining the content of the volatile matter in the coal samples that were used in the experiments.

TABLE 1

Volatile matter in the coal samples taken from selected mines of the Upper Silesian Coal Basin

Sample number	Mine	Volatile matter, V^{daf} [%]
1	Zofiówka mine	25.02
2	Szczygłowice mine	28.89
3	Brzeszcze mine	34.25
4	Sobieski mine	38.87

2.2. Research methods

The sorption experiments described in the article were carried out using a gravimetric system for the precise analysis of the size, dynamics and kinetics of gas sorption IGA-001 (*Intelligent Gravimetric Analyzer*), a Hiden Isochema device. This is advanced apparatus that measures the change in weight of a sample over time that is associated with sorption processes occurring in coal or other porous materials. Owing to the possibilities offered by the system, it is possible to conduct fully automated research with high precision.

Samples of lumps of coal were delivered to the laboratory, crushed and then sieved to obtain a 0.2-0.25 mm fraction. The samples prepared in this way were used for sorption experiments by the gravimetric method at 25°C under constantly controlled and stable conditions. Sorption

isotherms for each experiment were determined at 2 pressure points: 0.1 and 0.8 MPa. The sorption kinetics, on the basis of which the effective diffusion coefficient D_e was determined, were determined at a pressure of 0.1 MPa and presented values were taken into account for further consideration. The sample mass used for sorption experiments was approximately 150 mg.



Fig. 1. IGA-001 gravimetric system for gas sorption measurements

The volatile matter content was determined in accordance with the requirements of the Polish standard PN-G-04516 using the gravimetric method. This is based on measuring the loss of volatile decomposition products in solid fuel which is formed during heating without contact with air at 850°C for 7 minutes. The experiments used an analytical samples with a grain size of less than 0.2 mm. Volatile matter content was determined by converting the value obtained during laboratory experiments to a dry, ashless state:

$$V^a = \frac{(m_1 - m_2)100}{m_1 - m_3} - W^a \quad (1)$$

Where:

- V^a — Volatile matter content in the analytical sample [%]
- m_1 — crucible mass with lid and sample [g],
- m_2 — crucible mass with lid and non-volatile residue [g],
- m_3 — crucible mass with lid [g],
- W^a — moisture content in the analytical sample [%].

$$V^{daf} = V^a \frac{100}{100 - W^a - A^a} \quad (2)$$

Where:

- V^{daf} — volatile matter content in a dry, ash-free state [%],
- A^a — ash content in the analytical sample [%].

3. Application of gas diffusion models

The description of gas transport inside structures of porous solids, such as hard coal, is difficult due to the diversity of shape, size and the unknown nature of the pore network. Currently, in Polish underground mining conditions, the unipore model is used to determine the effective diffusion coefficient D_e (Dutka, 2017; Wierzbicki et al., 2017).

3.1. The unipore diffusion model

The unipore diffusion model assumes that the carbon matrix is homogeneous and consists of only one type of pore in which sorption and diffusion processes occur at the same rate. This analytical solution, which refers to Fick's second law, was also presented by Crank (1975) and Timofiejew (1967):

$$\frac{\partial c(r,t)}{\partial t} = \frac{D}{1+K_H} \nabla^2 c(r,t) = D_e \nabla^2 c(r,t), \quad D_e = \frac{D}{1+K_H} \quad (3)$$

Where:

- D — diffusion coefficient [m^2/s],
- D_e — effective diffusion coefficient [m^2/s],
- K_H — Henry's linear isotherm coefficient [$\text{mol/g} \cdot \text{bar}$],
- c — concentration of substance [mol/m^3],
- r — distance from the centre of the grain [m],
- t — time [s].

Using the necessary assumptions and simplifications (Wierzbicki & Skoczylas, 2010), the solution of equation (3) in specific initial and boundary conditions, described in available publications (Timofiejew, 1967; Crank, 1975; Pillalamarry et al., 2011), takes the following form:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_e n^2 \pi^2 t}{R_o^2}\right), \quad R_o = \frac{1}{2} \sqrt{\frac{2d_1^2 d_2^2}{d_1 + d_2}} \quad (4)$$

Where:

- M_t — mass of gas deposited in time t [g],
- M_∞ — total mass of gas deposited in grains [g],
- R_o — substitute grain radius [cm],
- d_1 and d_2 — grain boundary values for the examined grain class [cm].

A large proportion of the simplifying assumptions used in the unipore model are impossible to implement. Firstly, the grains cannot be considered to be perfectly spherical and the grain composition to be homogeneous. Another assumption states that the carbon matrix consists of only one type of pore. In fact, there are at least two different mechanisms related to methane diffusion from the microporous matrix and flows occurring in the voids and macropores (Keshavarz et al., 2017).

3.2. The bidisperse diffusion model

The second diffusion model considered in the article is the bidisperse model which was developed and described for the first time by Ruckenstein (1971). Its basic assumption is that the carbon matrix is a spherical particle containing the agglomeration of many small microporous spheres with macropores around microparticles (Dang et al., 2017), as shown in Fig. 2. (Ruckenstein et al., 1971).

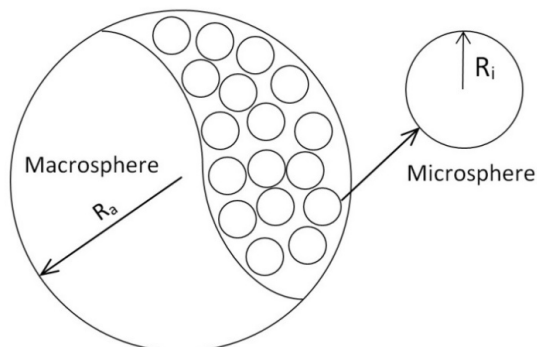


Fig. 2. Schematic representation of the carbon matrix with occurring micro- and macropores according to the assumptions of the bidisperse model

When considering the carbon structure as a bidisperse structure, diffusion processes and gas sorption should be considered in micro- and macropores as being competitive. The model presented also assumes that the isotherm equation is a linear function of pressure in which there is a step change in the gas concentration on the external surface of the adsorbent. Gas diffusion into micro and macrospheres are described by the equations below (Dang et al., 2017):

$$\frac{D_a \epsilon_a}{r_a^2} \frac{\partial}{\partial r_a} \left(r_a^2 \frac{\partial C_a}{\partial r_a} \right) = \epsilon_a \frac{\partial C_a}{\partial t} + S_a \frac{\partial C_{sa}}{\partial t} + 4\pi n R_i^2 \epsilon_i D_i \left(\frac{\partial C_i}{\partial r_i} \right)_{r_i=R_i} \quad (5)$$

Where:

- D_a — diffusion coefficient for macropores [cm²/s],
- D_i — diffusion coefficient for micropores [cm²/s],
- ϵ_a — macropore void fraction,
- ϵ_i — micropore void fraction,
- r_a — distance from the centre of macropores [cm],
- C_a — macropore fluid phase sorbate concentration [mol/cm³],
- C_{sa} — macropore adsorber phase concentration [mol/cm²],
- n — number of microspheres per unit volume of the macrosphere,
- R_i — microsphere radius [cm],
- S_a — macropore surface [cm²/cm³],
- t — time [s].

$$\frac{D_i \epsilon_i}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \frac{\partial C_i}{\partial r_i} \right) = \epsilon_i \frac{\partial C_i}{\partial t} + S_i \frac{\partial C_s}{\partial t} \quad (6)$$

Where:

- r_i — distance from the centre of micropores [cm],
- C_i — micropore fluid phase sorbate concentration [mol/cm³],
- C_s — micropore adsorber phase concentration [mol/cm²],
- S_i — micropore surface [cm²/cm³].

The solution for equations (5) and (6) was determined according to the boundary conditions that were applied by Ruckenstein (1971). Mathematical solutions are too complicated to be easily adapted to experimental data, which is why Ruckenstein (1971) provided a simplified solution. It assumes that the diffusion and adsorption process in macropores is much faster than in micropores, so the process was divided into two stages: faster, occurring in macropores and slower occurring in micropores. The equations taking into account the above assumptions are as follows:

$$\frac{M_a}{M_{a\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D'_a n^2 \pi^2 t}{R_a^2}\right) \quad (7)$$

Where:

- D'_a — effective diffusion coefficient for macropores [cm²/s],
- M_a — mass of gas deposited in macropores in time t [g],
- $M_{a\infty}$ — total mass of gas deposited in macropores [g],
- R_a — macrosphere radius [cm].

$$\frac{M_i}{M_{i\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D'_i n^2 \pi^2 t}{R_i^2}\right) \quad (8)$$

Where:

- D'_i — effective diffusion coefficient for micropores [cm²/s],
- M_i — mass of gas deposited in micropores in time t [g],
- $M_{i\infty}$ — total mass of gas deposited in micropores [g].

Based on the assumptions presented above, the final form of the equation for the bidisperse model taking into account diffusion and sorption processes occurring both independently in micro- and macropores is as follows:

$$\frac{M_t}{M_{\infty}} = \frac{\left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D'_a n^2 \pi^2 t}{R_a^2}\right) \right] + \frac{\beta}{3\alpha} \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D'_i n^2 \pi^2 t \alpha}{R_i^2}\right) \right]}{1 + \frac{\beta}{3\alpha}} \quad (9)$$

Where:

- α — dimensionless parameter specified:

$$\alpha = \frac{D'_i R_a^2}{D'_a R_i^2} \quad (10)$$

β — dimensionless parameter specified:

$$\beta = \left[3 \frac{(1 - \varepsilon_a) \varepsilon_i}{\varepsilon_a} \right] \left(\frac{D'_i R_a^2}{D'_a R_i^2} \right) \quad (11)$$

ε_a — macropore void fraction,

ε_i — micropore void fraction.

3.3. Mathematical formulation and model development

The numerical implementation of the unipore and bidisperse diffusion model was performed in the MATLAB computational environment, using equations (4) and (9), which were derived from the assumptions of Fick's second law. The infinite series was approximated as the sum of the first 100 terms, although previous studies show that even the use of the first 10 terms can provide satisfactory results (Crank, 1948; Mianowski & Marecka, 2009).

For the unipore model, curves $\frac{M_t}{M_\infty}(t)$ were determined with the assumed value of the coefficient being the quotient of the effective diffusion coefficient D_e and the equivalent square of the grain radius R_0 . The value of this coefficient is determined for each of the coal samples based on the sorption kinetics study described in chapter 2.2.

In the case of a more complex bidisperse model, an unknown set of parameters $\frac{D'_a}{R_a^2}, \frac{D'_i}{R_i^2}, \alpha, \frac{\beta}{\alpha}$ controlling the course of sorption and diffusion processes was found. The parameters were identified by fitting model curves with experimental data. An adjustment was made by minimizing the mean square error (MSE) of the models relative to the experimental results. The *Fmincon* solver implemented in MATLAB software, which enabled searching for a minimum of a non-linear function of many variables with constraints, was used as a tool to control the fitting process. Each of the parameters was searched in a range of values from 0 to 100. The magnitude of the mean square error enables the assessment of the validity of using the selected model. A value closer to 0 corresponds to a better fit with experimental data, which proves the validity of using the selected model.

4. Measurements results and discussion

For the purposes of the article, literature research was carried out. It was concluded that the unipore and bidisperse model were analysed in terms of their description of the phenomenon of methane sorption and diffusion in the porous structure of coal and the possibilities of their application in determining the effective diffusion coefficient. The relationship between maceral composition and coal type, and the course of diffusion and sorption processes has

also been described in the literature (Crosdale et al., 1998; Laxminarayana & Crosdale, 1999; Ceglarska-Stefańska & Zarębska, 2006; Pan et al., 2010; Olajossy, 2013; Dutka, 2017; Keshevarz et al., 2017).

From a mathematical point of view, the unipore model in many cases does not properly describe sorption kinetics, and the bidisperse model (Clarkson & Bustin, 1999; Cui et al., 2004; Pan et al., 2010; Dang et al., 2017; Li et al., 2019) provides a better fit. Clarkson & Bustin (1999) wrote that when assessing the applicability of one of the models, the porous structure of coal should be taken into account. They suggested that the unipore model is suitable for coals with a simple pore structure, assuming that they have a spherical and homogeneous structure, while the bidisperse model finds better application for coals with a complex porous structure.

Unlike a large part of the experiments described in the literature, which were carried out using the volumetric or manometric method, this article presents experiments carried out based on the gravimetric method. As a result, it was possible to precisely determine the methane sorption kinetics and the effective diffusion coefficient.

Based on the experiments, the relationship between the volatile matter content, which is directly related to the maceral composition and type of coal, and the methane diffusion and sorption process in the conditions of the Upper Silesian Coal Basin have been confirmed. In Fig. 3, the model runs are marked with a blue solid line, while the measured values are marked with red points corresponding to subsequent measurements made as described in chapter 2.2. The mean square error (MSE) value enables the assessment of the legitimacy of using the selected model.

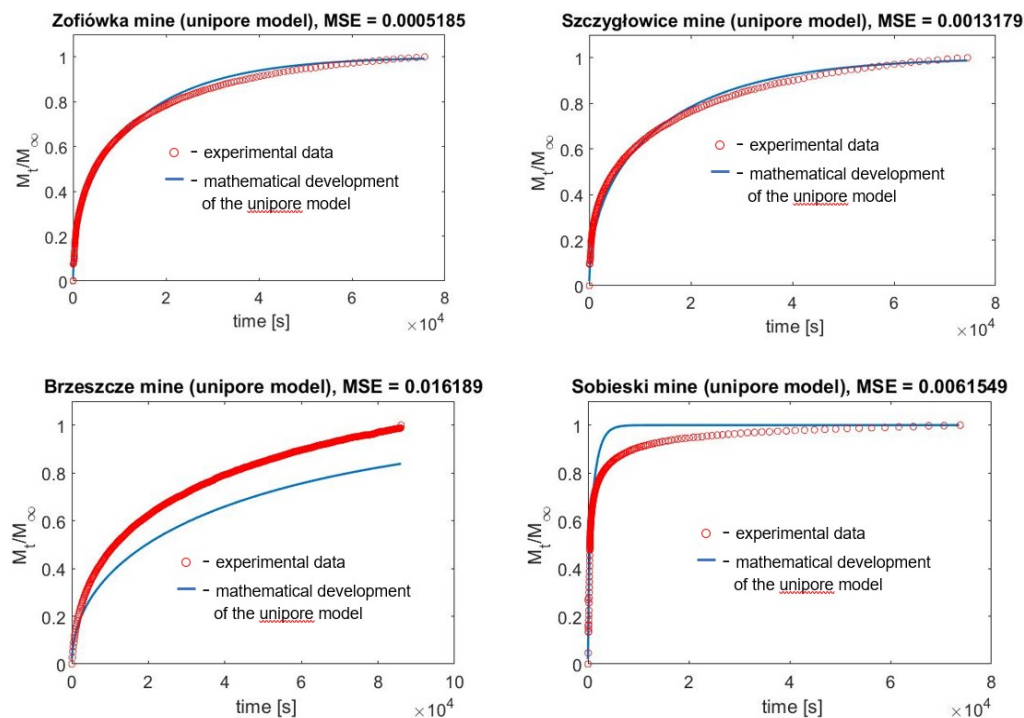


Fig. 3. Fitting of the mathematical development of the unipore model with experimental data

The Fig. 3. presents the results for the unipore model and indicate that only in the case of the Zofiówka and Szczygłowice mines the model run can be relatively well fitted to the experimental data. In the case of the two remaining experiments conducted for the Brzeszcze and Sobieski mines, this fit is not satisfactory, which is additionally confirmed by the high mean square error value, which is approximately 0.016 and 0.006. The relatively low volatile matter content, amounting to 25.02% for the Zofiówka mine and 28.89% for the the Szczygłowice mine, indicates their high degree of coalification. This conclusion is based on the dependency that the degree of coalification increases proportionally with the increase in the reflectivity of vitrinite, additionally an increase in the degree of coalification causes a decrease in the content of volatile matter in coal (Chruściel, 1986). The volatile matter content for the Brzeszcze and Sobieski mines was 34.25% and 38.86%, respectively, which indicates a lower degree of coalification. The dependency confirms the observations made in the work of other researchers. The process of the transformation of organic matter shapes the degree of expansion of the porous structure of coal, which directly affects the kinetics of sorption processes (Ceglarska-Stefańska & Brzóska, 1998; Laxminarayana & Crosdale, 2002). Table 2 presents the fitting parameters of the unipore model for a pressure of 0.1 MPa, when compared to the volatile matter content.

TABLE 2

The unipore diffusion model fitting parameters for the data for a methane adsorption rate at a pressure of 0.1 MPa

Mine	Pressure, [MPa]	R_o , [cm]	D_e , [cm ² /s]	V^{daf} , [%]
Zofiówka mine	0.1	0.011157	7.25E-10	25.02
Szczygłowice mine	0.1	0.011157	6.60E-10	28.89
Brzeszcze mine	0.1	0.011157	5.00E-10	34.25
Sobieski mine	0.1	0.011157	9.54E-09	38.87

The poor fit of the mathematical development of the unipore model with experimental data for coal samples from the Brzeszcze and Sobieski mines indicates their extensive porous structure. In connection with the above, it is necessary to consider their structure as bidisperse, in which the processes of the diffusion and sorption of gases in micro- and macropores occur simultaneously.

The application of the bidisperse model provides a very good fit of the solution to the experimental data for each of the coal samples, as shown in Fig. 4. In addition, this is confirmed by the low values of the mean square error, ranging from 6.45E-05 to 0.0014, which proves that this model is more suitable for describing sorption and diffusion processes for the analysed hard coal samples.

Table 3 summarizes the fitting parameters of the bidisperse model for a pressure of 0.1 MPa, when compared to the volatile matter content. The values of the effective diffusivity of macropores

$\frac{D'_a}{R_a^2}$, and the effective diffusivity of micropores $\frac{D'_i}{R_i^2}$ were also taken into account, and these

were then converted into the effective coefficient of diffusion of micro- and macropore values. The α parameter specifying the time scale ratio of processes occurring in micro- and macropores

and $\frac{\beta}{\alpha}$, which determines the sorption ratio in micro- and macropores in equilibrium, is also presented.

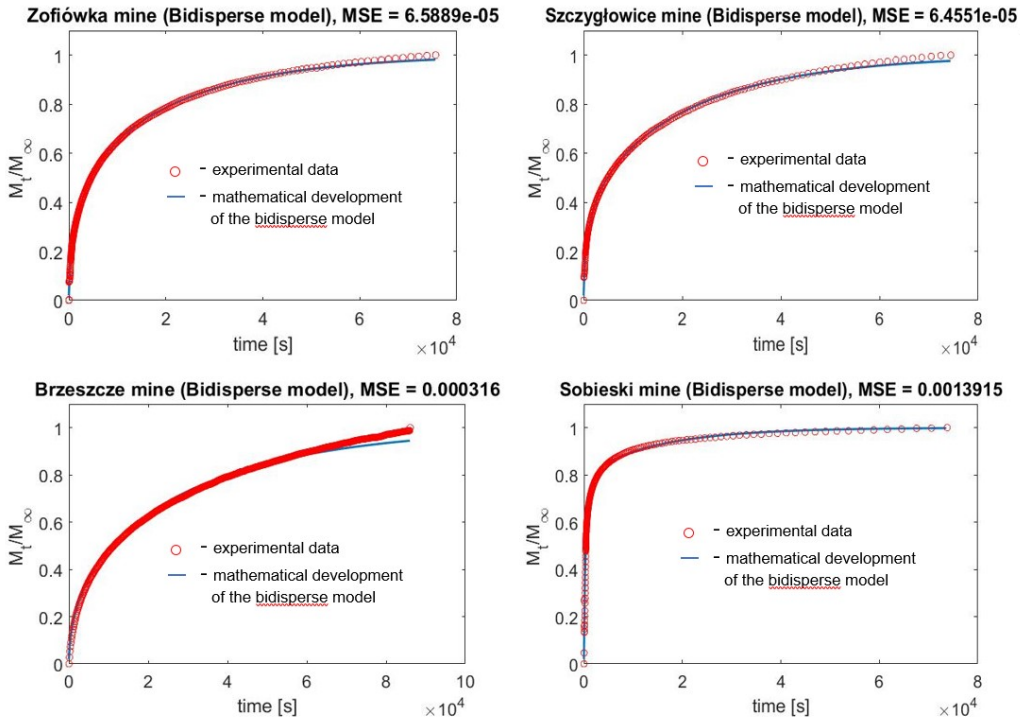


Fig. 4. Fitting of the mathematical development of the bidisperse model with experimental data

TABLE 3

The bidisperse diffusion model fitting parameters for the data on the methane adsorption rate at a pressure of 0.1 MPa

Mine	P [MPa]	$\frac{D'_a}{R_a^2}$ [s ⁻¹]	$\frac{D'_i}{R_i^2}$ [s ⁻¹]	α	$\frac{\beta}{\alpha}$	D'_a [cm ² /s]	D'_i [cm ² /s]	V^{daf} [%]
Zofiówka mine	0.1	4.4359e-06	0.0206	0.0016	0.6163	5.52e-10	2.56e-06	25.02
Szczygłowie mine	0.1	4.2389e-06	0.0103	0.0110	0.4584	5.28e-10	1.28e-06	28.89
Brzeszcze mine	0.1	2.6855e-06	4.6013e-06	0.6157	99.0097	8.57e-10	1.47e-09	34.25
Sobieski mine	0.1	1.3777e-04	0.0012	0.0052	1.2665	1.71e-08	1.48e-07	38.87

5. Conclusion

This research shows that for some coal experiments, the bidisperse model is much better suited to the actual sorption kinetics. This justifies the need to conduct research on the scope of the applicability of the compared models. Preliminary results indicate a relationship between the degree of coalification resulting from the volatile matter content and the processes of sorption and diffusion of methane on hard coal. The better fit of the bidisperse model suggests that in

order to properly determine the values of effective diffusion coefficients, coal structure should be considered as a complex matrix with at least two different mechanisms (connected to each other) related to the diffusion of methane from the microporous matrix and flows occurring in the voids and macropores.

The unipore and bidisperse diffusion models was used for interpreting and determining the value of parameters related to the course of sorption in hard coal in the conditions of the mines of the Upper Silesian Coal Basin. The unipore model provides a good fit and can be used for coals with a high degree of coalification which show a low volatile matter content. In the case of coals with a low degree of coalification and high content of volatile matters, it is necessary to use a bidisperse model and consider sorption processes as being simultaneous in micro- and macropores.

Enabling a choice of the sorption kinetics model may be important for the quality of numerical modelling of these processes and for the assessment of rock and gas outburst hazard.

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