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KINETICS OF GASEOUS SORBATE ACCUMULATION AND EMISSION PROCESSES FROM A POROUS MEDIUM – IS THE DIFFUSION COEFFICIENT A MATERIAL CONSTANT?

The kinetics of sorption and diffusion processes in porous materials significantly influence applications such as greenhouse gas capture, toxic gas removal, and geological storage. This study investigates whether the diffusion coefficient, a critical parameter in describing these processes, can be treated as a material constant. Experimental analyses were conducted using hard coal samples subjected to methane sorption under controlled conditions. Numerical and analytical models were developed, incorporating linear and Langmuir sorption isotherms, to simulate the diffusion and sorption processes. Results indicate that assuming a linear isotherm allows for satisfactory modelling in low-density sorbate regions but introduces artefacts at higher densities, where the Langmuir isotherm provides superior accuracy. The numerical model, validated against analytical solutions, demonstrates high precision in extracting diffusion coefficients and isotherm parameters, highlighting the interdependence of sorption kinetics and equilibrium conditions. These findings emphasise the need for advanced modelling techniques to accurately characterise diffusion in complex porous systems and establish the diffusion coefficient as a robust material property.

Keywords: Porous materials; greenhouse gas (GHG); sorption; diffusion coefficient; geological storage; Langmuir isotherm

1. Preface

Experimental analysis of adsorption processes is most frequently based on studies of the established equilibrium states between the external sorbate and the sorbent grains [1,2]. The kinetics

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of processes leading to these equilibrium states are studied much less frequently [3]. These are more complex tasks. Their analysis, however, is of great importance for a number of applications where the speed of the process is crucial [4]. An important group of such applications concerns the issues of adsorptive capture of gaseous components from a gas-air mixture [5]. This is directly related to the dynamically developing area of greenhouse gas or toxic gas capture from various gas streams [5-12]. The knowledge of the process of sorbate gas emission from rocks originally saturated with it is also important for the analysis of the efficiency of energy raw materials extraction. It also determines the possibility of geological storage of greenhouse gases [13-17].

Measurements to determine the diffusion coefficient are most frequently conducted on a granular bed of crushed sorbent surrounded by sorbate, the density of which changes in a controlled manner. The interpretation of measurement results consists of comparing the observed process of sorbate accumulation or emission with the prediction of the mathematical model of the studied process [18-22].

Normally, a model is selected that allows for many simplifications, one of which is the assumption that the sorption isotherm for the sorbent-sorbate system is linear. Thanks to this assumption, the diffusion equation is sufficient to describe the integrated sorption and diffusion processes, in which the diffusion coefficient is replaced by the effective diffusion coefficient, the value of which is equal to the quotient of the diffusion coefficient and the coefficient of the linear sorption isotherm. Additionally, isobaric measurement conditions with a step change in the concentration (pressure) of the gaseous sorbate are often assumed. Consequently, this imposes strict requirements regarding the measurement technique. Another simplification is replacing the real grain shapes with a symmetrical spherical grain. Attempts to eliminate this last simplification require separate considerations. The advantage of combining the assumptions of a linear sorption isotherm and grain sphericity is the possibility of using an analytical solution of the diffusion equation. Analogous analytical solutions are also known for the thin layer and the cylinder [23,24].

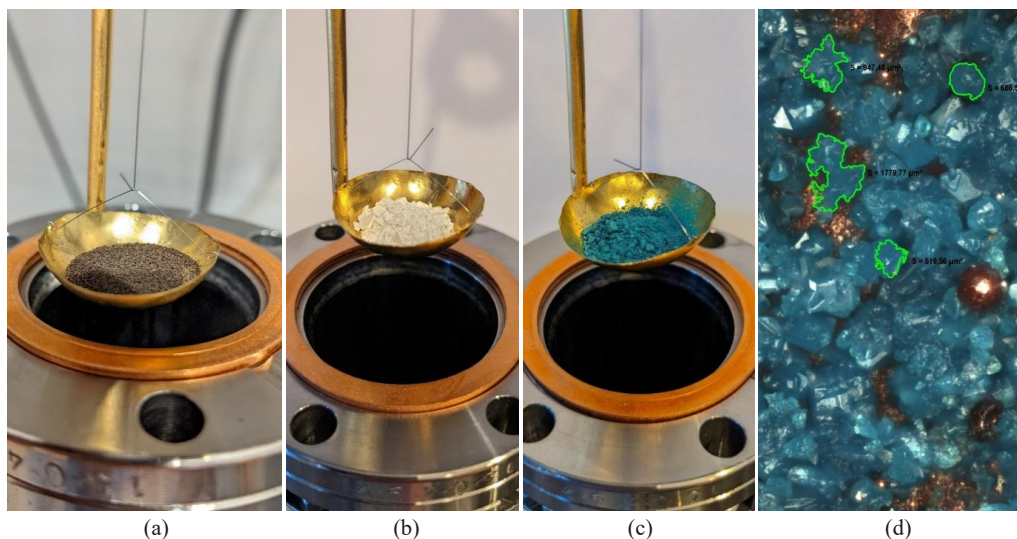


Fig. 1. (a) Grainy sample of coal; (b) Granules of MOF UiO-66 material [29]; (c) Granules of MOF HKUST-1 material [30]; (d) Granules of MOF HKUST-1 material [30]

Studies of sorption (diffusion) kinetics are conducted on many classes of materials. These are both natural materials, such as, for instance, coal or other minerals (Fig. 1(a)) [18,25,26] as well as synthetic porous materials, most often obtained in the form of powders (Fig. 1(b) and 1(c)) [27,28], or equivalent layers (Fig. 1(d)), whose granules have a statistically defined geometry.

2. Combined transport and sorption processes – the physics of the phenomenon

The word adsorbate will refer to sorbate molecules bound within the sorbent. Most of the adsorbate particles, as a result of surface interactions, are immobilised on the pore walls. Some of them constitute a quasi-gaseous mobile fraction filling the interior of the sorbent pores. Mobile fraction particles are capable of diffusion transport. The state of the bound adsorbate and the state of its mobile fraction will be determined by their densities ρ_a and ρ_m , expressed in $[\text{mol}/\text{m}^3]$, relating to an elementary small fragment of the sorbent. At the sorbent boundary, the density of the mobile fraction ρ_m is equal to the ρ_g density of the gaseous sorbate in the environment. In the unsteady state, the local densities ρ_a and ρ_m depend on the position in the sorbent.

The local equilibrium of ρ_a and ρ_m is defined by the sorption isotherm:

$$\rho_b = F(\rho_m) \quad (1)$$

We assume that at every point in the sorbent, regardless of the processes taking place, a local equilibrium between the adsorbate and its mobile fraction is maintained. It is an extension of the concept of sorption equilibrium, which is applied to the sorbent grain after full saturation with the adsorbate.

If the equilibrium (1) is disturbed, for example, due to diffusional transport of the mobile fraction, an exchange of the mobile fraction particles and the particles bound on the pore walls takes place. This leads to the restoration of the local sorption equilibrium (1). The rate of disruption of the local sorption equilibrium associated with diffusion is considered to be much lower than the rate of exchange of sorption-bound and mobile particles.

As a result, we assume that the local equilibrium (1) returns in a follow-up manner. This assumption essentially means that the time dependencies refer not to sorption but to diffusion.

For the purposes of model analyses, we select an elementary small fragment of the sorbent, with a volume δv , which, at the moment t_0 , contains the adsorbate with density $\rho_a(t_0)$ and mass $M(t_0) = \delta v \rho_a(t_0)$.

Let as a result of the diffusion of the mobile sorbate, at the moment $t_0 + dt$, the density of the mobile fraction of the adsorbate in δv changes by $\delta \rho_m$. This change causes a change in the total density of the adsorbate, also by $\delta \rho_m = \delta \rho_a$. According to Fick's law, the change is:

$$\begin{aligned} \delta \rho_a &= dt D^* \Delta^2(\rho_m) d\rho_b = dt D \nabla^2(\rho_m) \\ dM &= dt D \nabla^2(\rho_m) = d\rho_m \frac{dF(\rho_m)}{d\rho_m} \end{aligned} \quad (2)$$

where, D^* is the effective diffusion coefficient.

After the exchange of particles and return to equilibrium, the increase in the density of the mobile sorbate is corrected:

$$\delta\rho_a = dtD^*\nabla^2(\rho_m) = \frac{d}{d\rho_m}F(\rho_m)\delta\rho_m \quad (3)$$

$$\delta\rho_m = \frac{dtD^*\nabla^2(\rho_m)}{\frac{d}{d\rho_m}F(\rho_m)} \quad (4)$$

In the case of a linear isotherm of the form:

$$\rho_a = K_H\rho_m \quad (5)$$

we get:

$$\begin{aligned} \delta\rho_m &= \frac{dtD^*\nabla^2(\rho_m)}{K_H}d\rho_m = \frac{dtD\nabla^2(\rho_m)}{K_H} = dtD^*\nabla^2(\rho_m) \\ d\rho_m &= \frac{D}{H}dt^*\nabla^2(\rho_m) \end{aligned} \quad (6)$$

In this simplest case (6), the modified diffusion equation is sufficient to describe the combined sorption and diffusion processes.

The kinetics of the accumulation and emission processes of gaseous sorbate from a porous sorbent are determined by:

- diffusion coefficient related to the transport of the mobile fraction of the gaseous adsorbate within the sorbent,
- An adsorption isotherm defines the relationship between an adsorbate and its mobile fraction in a state of local sorption equilibrium,
- the nature of changes in the sorbate state at the sorbent boundary,
- size and shape of sorbent grains/granules,
- temperature.

Dynamic processes of sorbate sorption and diffusion in the pore structure of the sorbent are most often provoked by the change of sorbate density outside the grain. As a result of the mechanisms discussed above, at individual moments of time the distribution of the mobile sorbate density inside the grain (Fig. 2) of the porous sorbent is established, which tends to achieve equilibrium with the sorbate density outside the grain.

2.1. Analytical model of diffusion and sorption

If we assume linearity of the sorption isotherm, the equation describing the sorption process comes down to the diffusion Eq. (6). Analytical solutions of Eq. (6) were found for different sorbent grain geometries. In this paper, we will construct models based on spherical sorbent grain.

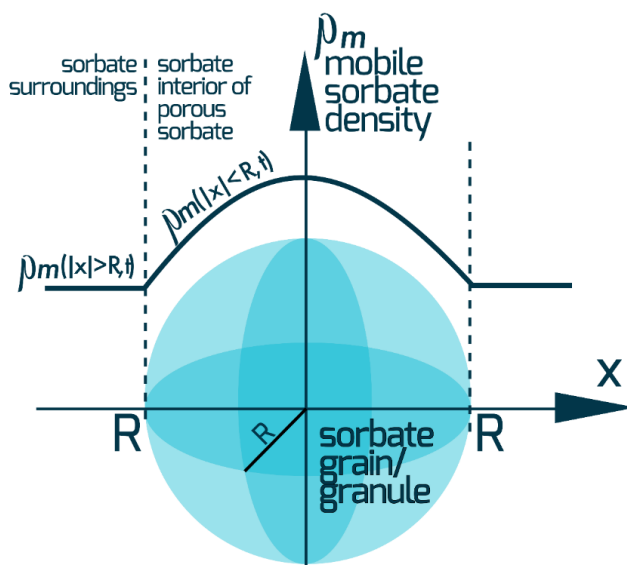


Fig. 2. Density distribution of mobile sorbate inside and outside the sample grain

In the case of a sphere with radius R , Eq. (6) takes the form:

$$\frac{\partial u}{\partial t} = D^* \frac{\partial^2 u}{\partial r^2}, \quad u = r \cdot \rho_a(r, t) \quad (7)$$

where: r is the distance from the centre of the spherical grain, $\rho_a(r, t)$ and $\rho_m(r, t)$ is the density of the adsorbate and its mobile fraction along the grain radius

The form of the solution to Eq. (6) depends on the nature of the changes in the sorbate density $\rho_a(R, t)$ that occur on the grain surface. If we assume a step change in density from $\rho_a(R, 0) = 0$ to $\rho_a(R > 0) = \rho_{g0}$ and when at the moment $t = 0$ the density of the mobile fraction of the adsorbate is ρ_{g1} , the solution (7) determines the density distribution of the mobile adsorbate fraction with the formula:

$$\frac{\rho_g(r, t) - \rho_{g1}}{\rho_{g0} - \rho_{g1}} = 1 - \frac{2R}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \exp\left(-t \frac{D^* (\pi n)^2}{R^2}\right) \sin\left(\frac{r \pi n}{R}\right) \quad (8)$$

where: constants ρ_{g1} and ρ_{g0} determine the values of the average sorbate density in the grain before and after completing the process.

The mass $M(t)$ of the substance accumulated in the spherical grain tends to a limiting value M_0 according to the formula:

$$\frac{M(t)}{M_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2 \pi^2 D^* t}{R^2}\right) \quad (9)$$

Solution (9) is often used in scientific papers. In addition, Timofeyev provided a much simpler engineering method for determining the effective diffusion coefficient (Timofeyev, 1967). By solving Eq. (9) for the time instant at which the mass of the gas is half of the final mass:

$$\frac{6}{\pi^2} \left(\exp\left(\frac{-D^* \cdot \pi^2 \cdot t}{R^2}\right) + \frac{1}{2^2} \exp\left(\frac{-2^2 D^* \cdot \pi^2 \cdot t}{R^2}\right) + \frac{1}{3^2} \exp\left(\frac{-3^2 D^* \cdot \pi^2 \cdot t}{R^2}\right) + \dots \right) = \frac{1}{2} \quad (10)$$

One can obtain the so-called Timofeyev's formula, which is the basis of the engineering method for determining the diffusion coefficient:

$$D^* = \frac{0.308 \cdot R^2}{\pi^2 \cdot t_{\frac{1}{2}}} \quad (11)$$

where: $t_{1/2}$ is the half time of the process [s].

The application of the model described by formulas (8), (9), (11) requires the use of measurement methods and research devices that can meet the difficult condition of a step change in the sorbate density. If we decide on gradual changes in the sorbate density at the grain boundary according to the formula:

$$\theta(t) = \rho_{g0}(1 - e^{-\beta t}) \quad (12)$$

We mitigate the conditions imposed on the measuring apparatus. In this case, changes in the density distribution of the mobile adsorbate $\rho_g(r, t)$ and temporal changes in the sorbate content $M(t)$ in the grain are described by the formulas:

$$\frac{\rho_g(r, t)}{\rho_{g0}} = 1 - \frac{R}{r} \exp(-\beta t) \frac{\sin\left(\sqrt{\frac{\beta R^2}{D}} \frac{r}{R}\right)}{\sin\left(\sqrt{\frac{\beta R^2}{D}}\right)} - \frac{2\beta R^3}{\pi D r} \sum (-1)^n \frac{\exp\left(\frac{D n^2 \pi^2 t}{R^2}\right)}{n \left(n^2 \pi^2 - \frac{\beta R^2}{D}\right)} \sin\left(\frac{n \pi r}{R}\right) \quad (13)$$

$$\frac{M(t)}{V \rho_{g0}} = 1 - \frac{3D}{\beta R^2} \exp(-\beta t) \left[1 - \sqrt{\frac{\beta R^2}{D}} \cot \sqrt{\frac{\beta R^2}{D}} \right] + \frac{6\beta R^2}{\pi^2 D} \sum \frac{\exp\left(\frac{-D n^2 \pi^2 t}{R^2}\right)}{n^2 \left(n^2 \pi^2 - \frac{\beta R^2}{D}\right)} \quad (14)$$

These formulas, despite their apparent complexity, can be easily implemented in popular programming languages.

2.2. Numerical model of diffusion and sorption

The numerical model divides the process time into a sequence of time segments of length dt . In order to optimise the calculation time, the length of segments dt may be extended during the described process. We take into consideration the fact that the rate of processes within the grain significantly slows down as its sorption capacity is filled with sorbent. The grain is also divided into spheres, between which flows are calculated.

2.3. Geometric grain division

To implement the numerical model, we divide the spherical grain by concentric spheres with radii $r[i]$, $i = 0, 1, \dots, N$ (Fig. 3). The radii of the spheres change evenly with a step R/N from $r[0] = R$ to $r[N] = 0$. The density distribution of the mobile fraction along the grain radius is represented by the densities $\rho_m[i](t)$ at the locations of the spheres. At the grain boundary, the density $\rho_m[0]$ equalises with the density of the outer sorbate.

To the spheres $[i > 0]$ we assign an environment covering the area between spheres $r[i - 1]$ and $r[i + 1]$.

In the case of the boundary sphere $r[0] = R$, the environment includes the area between the spheres $r[0] = R$ and $r[1]$. The sphere $r[N]$ has been reduced to a point and a zero neighbourhood.

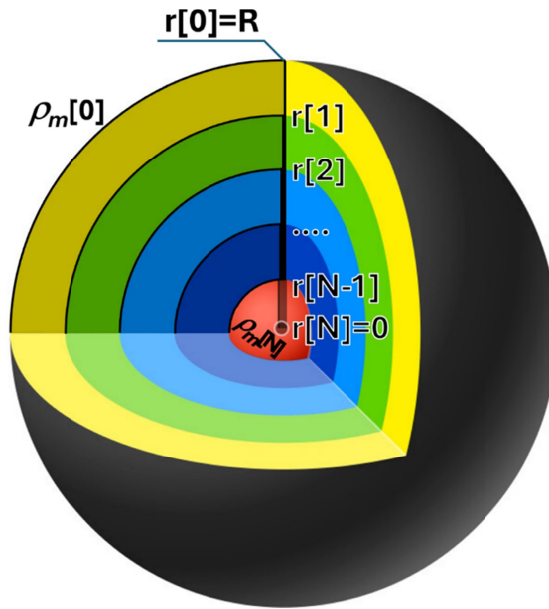


Fig. 3. The spatial division scheme of the sorbate grain for the needs of the numerical model

We assume that at the start of the next time segment dt , we know the density $\rho_m[i]$ of the mobile fraction of the adsorbate. At the grain boundary, the density $\rho_m[0]$ equalises with the density of the external gaseous sorbate.

2.4. Sorbate flows

To estimate the transfer of mobile sorbate occurring during the step dt through the grain-dividing spheres, the density gradients of the mobile fraction at the sphere locations need to be estimated.

At the grain boundary $r[0]$ this gradient is approximated by the quotient:

$$\frac{d}{dr} \rho_m [0] \frac{N(\rho_m [1] - \rho_m [0])}{R} \quad (15)$$

For spheres from $r[1]$ to $r[N-1]$ we use the quotient approximation:

$$\frac{d}{dr} \rho_m [i] \frac{N(\rho_m [i+1] - \rho_m [i-1])}{2R} \quad 1 < i < N-1 \quad (16)$$

For the sphere $r[N]$ reduced to a point we assume:

$$\frac{d}{dr} \rho_m [N] 0 \quad (17)$$

As a result of the density gradient, the mobile sorbate particles are transported through subsequent spheres. If we neglect the changes that will occur during the time dt , and if we accept the precision of the above approximations (15,16,17), a sorbate transfer $q[i]$ flows through the sphere $[i]$ during the time dt :

$$q[i] \approx \frac{d\rho_m [i]}{dr} D^* s[i] dt \quad (18)$$

where: D^* – is the effective diffusion coefficient, $s[i]$ – is the surface area of a sphere $r[i]$.

Determining the change in density that will occur in time $s[i]$ in a sphere $r[i]$ requires examining the changes that occur in its environment, limited by the neighbouring spheres $r[i-1]$, $r[i+1]$. By balancing transfers through the boundaries of the environment, we find a change in the content of such an environment. This change, although carried out by the mobile fraction, affects the entire adsorbate. It determines the change $d\rho_a[i]$ in the average density of the adsorbate in the sphere environment $r[i]$:

$$d\rho_a = \frac{q[i-1] - \rho[i-1]}{v[i]} \quad (19)$$

where: $v[i]$ – is the volume between spheres $r[i-1]$ and $r[i+1]$.

The flows of the mobile fraction disturb the original local sorption equilibrium (1). The continuous equalisation of the sorption equilibrium requires changes in the sphere environment $r[i]$:

$$d\rho_a = d\rho_a [i] = d\rho_m \frac{dF}{d\rho_m} \rightarrow d\rho_m = d\rho_a \left(\frac{dF}{d\rho_m} \right)^{-1} \quad (20)$$

which we attribute to the center of the environment $d\rho_m[i]$.

The modification that takes place in time dt consists in increasing the densities $\rho_m[i]$ assigned to subsequent spheres $[i]$ by the correction value $d\rho_m$ (20). For the grain centre $r[N]$, we assume that $d\rho_m[N] = d\rho_m[N-1]$.

This simplification is justified by the fact that the volume of the sphere $r[N-1]$ surrounding the grain centre is a small and therefore insignificant part of the grain volume. When $N = 100$, it is 0.001% of the grain volume.

The repeated procedure of determining and taking into account the correction $d\rho_m$ determines the evolution of the density distribution within the grain. The change in grain content is obtained by summing the transfers of mobile sorbate (18) across the grain boundary. The derivative of the

isotherm $\frac{dF(\rho_m)}{d\rho_m} \frac{dF(\rho_m)}{d\rho_m} \rho_m$, depends on its type.

If we accept the linear isotherm $\rho_a = h * \rho_m$, the derivative takes a constant value

$$dF \frac{(\rho_m)}{d\rho_m} \rho_m = h \quad (21)$$

If it is necessary to use the Langmuir isotherm, the derivative is:

$$\rho_a = F(\rho_m) = \frac{hA\rho_m}{1 + \rho_m A} \rightarrow \frac{dF}{d\rho_m} = \frac{hA}{(1 + \rho_m A)^2} \quad (22)$$

3. The numerical model with linear sorption isotherm

The numerical model was developed according to the described scheme in Python. Working on the numerical model was preceded by tests aimed at confirming its substantive correctness.

In the case of modelling the phenomenon of diffusion and sorption, it is possible to clearly confirm the correctness of the prepared numerical model by demonstrating its convergence with the analytical solution (Fig. 4), assuming the simplest conditions for the course of the modelled phenomenon. These conditions constitute a significant limitation, but are necessary if we are to use analytical models. The most important limitation is the need to use a linear sorption isotherm, which leads to the risk of errors.

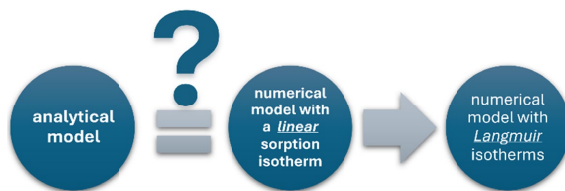


Fig. 4. The concept of confirming the correctness of the numerical model

3.1. Convergence of the analytical solution and the numerical model

In order to compare the results of the numerical model with the analytical solution, the kinetics of emission (desorption) of gaseous sorbate from spherical sorbent grains with radius

$R = 0.125$ mm were generated. The values of the diffusion coefficient and isotherm parameters were selected as typical for the activated carbon-methane system 2×10^{-6} m²/s. Desorption occurred under the conditions of a step change in ambient density from 180 to 0 mol/m³.

In order to generate the required density distribution along the radius of a spherical grain, we will use the analytical model described by formula (8) and, in parallel, an appropriate numerical model. In the weakly convergent sum of the series from formula (8), $k = 10000$ terms of the series expansion are taken into account. The grain in the numerical model was divided into $N = 100$ spheres. The time step was $dt = 10^{-8}$ s.

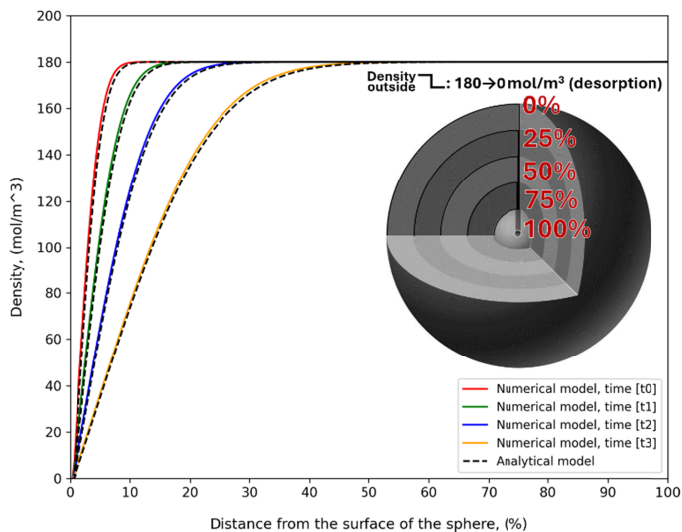


Fig. 5. Comparison of results from the analytical and numerical models, $t = 2, 4, 10$ and 30 s

Examples of the density distribution of the mobile sorbate fraction captured at selected time moments ($= 2, 4, 10$ and 30 s) are presented in the graphs in Fig. 5. We observe that after 2 seconds, the effects of the gas emission process cover only about 10% of the outer layer of the spherical grain. After about 30 seconds, the zone of intensive gas transport reaches about 40% of the outer part of the grain. However, the most important goal of presenting these results is to evaluate the convergence of numerical and analytical solutions. It should be noted that the numerical and analytical results in the case of the linear isotherm are satisfactorily convergent. This proves the correctness of using the numerical procedure despite numerous simplifications and justifies its application in more advanced versions, without simplifications.

3.2. Approximation of measurement data with an analytical and numerical model with a linear sorption isotherm

Experimental studies of the kinetics of gaseous sorbate accumulation/emission from a porous sorbent are aimed at determining the value of the diffusion coefficient and the asymptotic value of sorption. The diffusion coefficient is a material constant that characterises the porous

medium – gas system in terms of the gas transport rate. Determining the exact value of the diffusion coefficient is difficult, which is a consequence of many assumptions of the model description. This value is very sensitive to the parameters of conducting the experiment and the sample preparation technique.

Extraction of the diffusion coefficient value requires comparing the measurement results of the kinetics of accumulation/emission of the crushed grain bed with the results generated by the analytical or numerical model. The analytical model describes the saturation of a spherical grain in the case of accepting a linear isotherm. It is not possible to analytically solve the Fick diffusion equations with a factor representing sorption if the sorption isotherm is more complex than linear. For the purpose of the model, the experiment requires the selection of a very narrow grain class of the tested material. The grain shape geometry is assumed to be spherical. Most often, a step change in the conditions describing the state of the gaseous sorbate surrounding the porous medium is assumed, which usually means an increase from vacuum to a relatively low pressure value in order to remain as close as possible to the linear region of the sorption isotherm.

By manipulating the model parameters using an optimising algorithm, we fit the model to the measurement results. The measure of the perfection of the obtained fit is the sum of the squares of the deviations, or an analogous measure of divergence.

The analysed process is the response of the system to the change of external conditions from vacuum to low sorbate densities (Figs. 8-10), or in the opposite direction. Extended data extraction with nonlinear sorption isotherm coefficients (e.g. Langmuir) is not possible in this case – it requires simultaneous analysis of several sorption points.

The measurement data used to extract the diffusion coefficient come from the IGA-001 device (Fig. 6). This device is classified as a sorption balance. The sample placed on the balance pan (Fig. 7) in a sealed reactor is subjected to changes in the density (pressure) of the surrounding



Fig. 6. IGA-001 measuring device

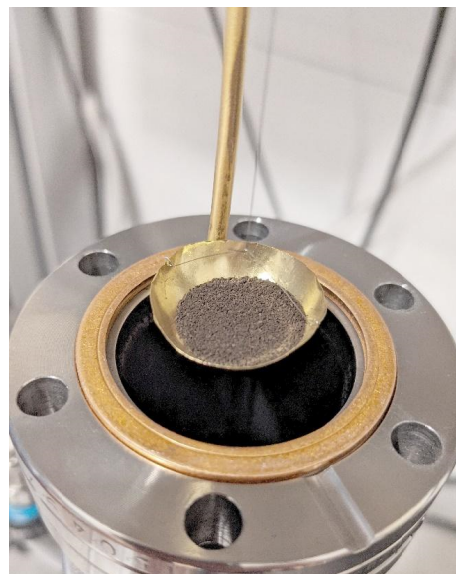


Fig. 7. Research material on the pan of the measuring device

gas. The changes in the sample mass as a result of sorption are recorded. The measurement is carried out in isothermal and quasi-isobaric conditions. The changes in the pressure surrounding the sample take place with an intensity of up to 300 mbar/s. After reaching the target pressure, the pressure value is stabilised.

The research material consisted of three samples of hard coal, sieved to a narrow grain size of 0.20-0.25 mm. The measurement was preceded by degassing the sample at a temperature of 80°C for 24 hours in a deep vacuum (turbomolecular pump). The experiment was conducted at 40°C. It consisted of 3 sorption phases, each triggered by a change in methane pressure: 0-0.1 MPa, 0.1-0.5 MPa, 0.5-1.5 MPa.

The analytical model, as well as the numerical model with a linear sorption isotherm, allows for approximating only the first sorption phase for the lowest density values.

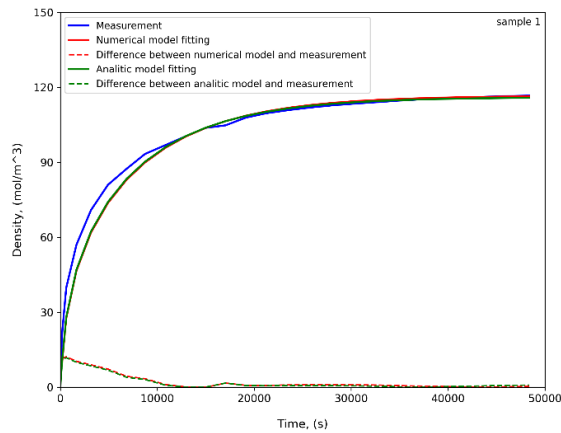


Fig. 8. Approximation of the first measurement phase (0-0.1 MPa, sample 1) with the analytical and numerical model

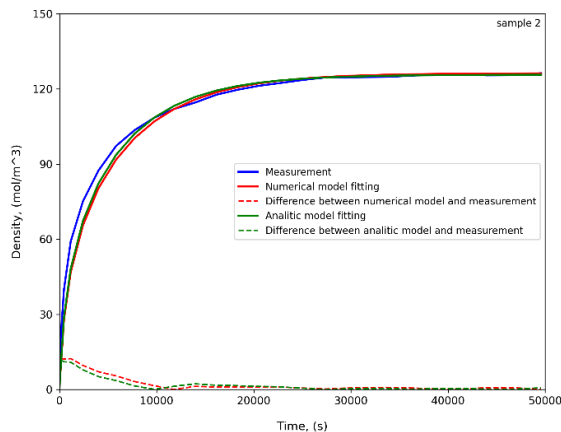


Fig. 9. Approximation of the first measurement phase (0-0.1 MPa, sample 2) with the analytical and numerical model

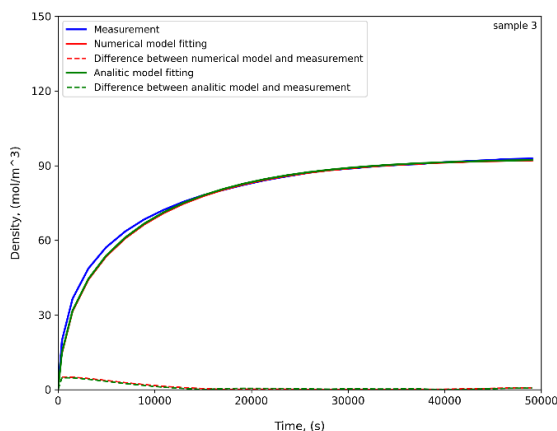


Fig. 10. Approximation of the first measurement phase (0-0.1 MPa, sample 3) with the analytical and numerical model

Using an analytical and numerical model based on a linear sorption isotherm, the extraction of the diffusion coefficient value from the measurement data of a single emission/accumulation kinetics (Figs. 8-10) was performed. The procedure consisted in algorithmic fitting of the diffusion coefficient and the asymptotic value of the kinetics. The gradient method was used, and the values were optimised based on the search for the minimum of squared deviations between the measured and modelled values.

TABLE 1

Approximated diffusion coefficients using analytical and numerical models with linear isotherm

Sample no	Numerical model fitting, D (m ² /s)	Analytic model fitting, D (m ² /s)	Relative difference, (%)
sample 1	5.47e-13	5.47e-13	0.001
sample 2	6.33e-13	6.36e-13	0.580
sample 3	3.40e-13	3.42e-13	0.619

The fit of the model parameters to the measurement data is excellent. The comparison of diffusion coefficient values derived from the measurement data using the analytical model with those obtained from the numerical model employing a linear sorption isotherm shows strong agreement between the two approaches. The relative differences are less than 1%, further validating the accuracy and reliability of the proposed numerical model.

4. Numerical model with Langmuir sorption isotherm

The acceptance of the linear isotherm is most often possible for sorption/desorption kinetics at low sorbate densities. However, in a wider range of sorbate densities for the dominant group of sorbents, the sorption isotherm can be described using the Langmuir formula or another nonlinear isotherm. In the case of sorbate transport, which is the effect of changing conditions surround-

ding the sample, in the range of low density values, the differences between both isotherms are usually small. The differences between sorption isotherms become difficult to accept when we analyse the sorption process conducted at higher sorbate densities. These increasing differences are illustrated by comparing the Langmuir isotherm with its linear simplifications (Fig. 11).

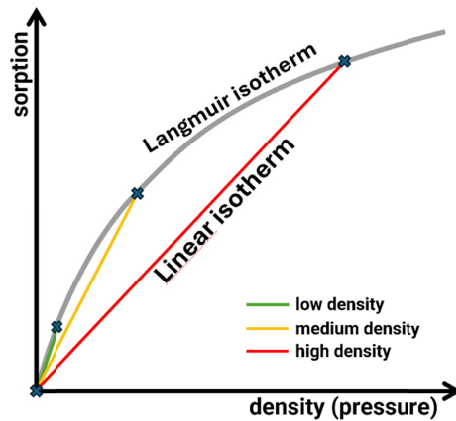


Fig. 11. Typical regions of convergence of the Langmuir and linear isotherms

The described numerical procedure works with any form of sorption isotherm. An example of application for the linear Henry isotherm and the Langmuir type isotherm is shown in Figs. 12-14. Fig. 12 shows the modelling of changes in the density distribution of gaseous sorbate during sorption (step change of external conditions from density 0 to density 180 mol/m³), captured at

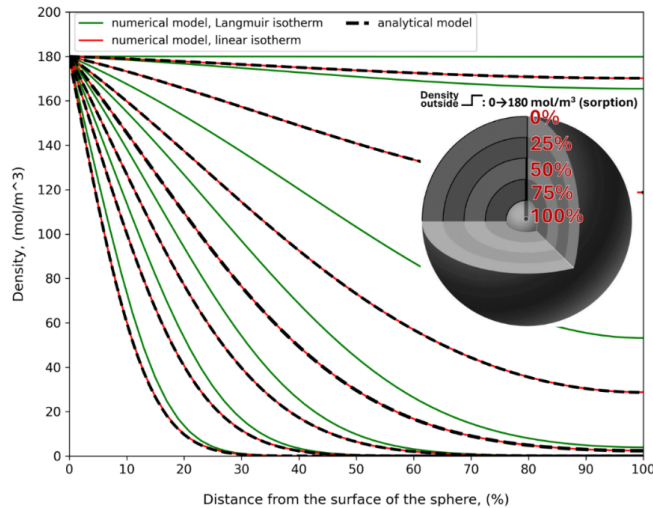


Fig. 12. Comparison of results from the analytical and numerical model with the linear and Langmuir isotherms

successive moments. The results obtained using the numerical model are marked with continuous lines: green for the Langmuir isotherm, red for the linear isotherm. Additionally, the dashed line indicates the results from the analytical solution.

The time moments that were analysed were seconds: 180, 620, 1300, 2500, 4500, 12000 and 39000 s. The convergence of the analytical model with the numerical model, using the linear isotherm, is clearly visible. This is the expected result, which confirms the correctness of the numerical model used. The same numerical model, adapted to the Langmuir isotherm, generates results that are significantly different from the results given by the models corresponding to the linear isotherm. These results indicate that the potential improvement in quality of the generated results, for materials with the Langmuir type sorption isotherm, is significant.

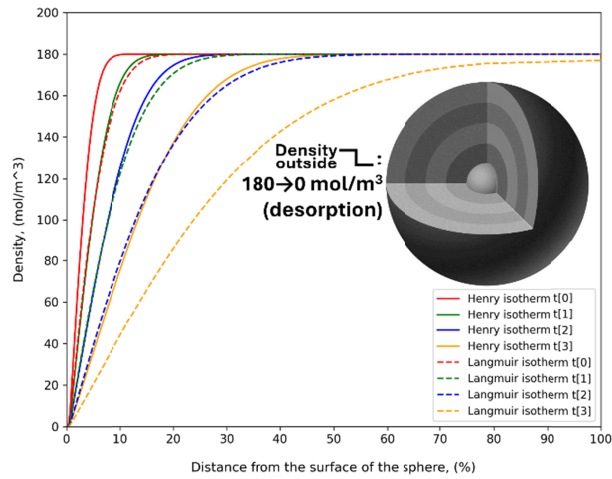


Fig. 13. Comparison of results from the analytical and numerical model

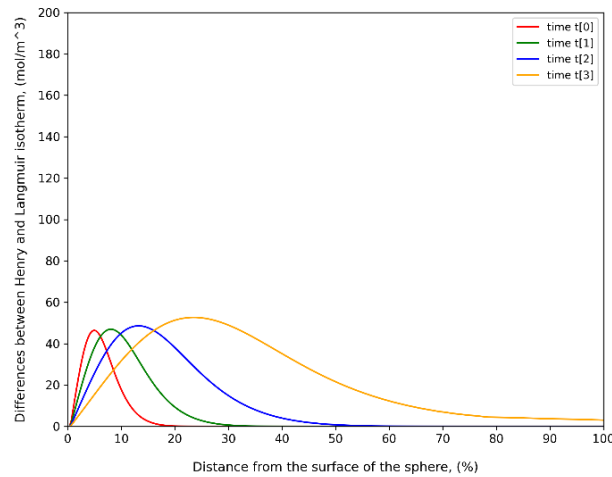


Fig. 14. Differences in results from the analytical and numerical model

The next graph (Fig. 13) presents the results of modelling the changes in the density distribution of the gaseous adsorbate in a spherical grain ($R = 5$ mm) during desorption (change of external conditions from density 180 to density 0 mol/m³), captured at subsequent moments (0.07 s, 0.52 s, 5.2 s, 50.2 s). A linear isotherm with a slope of $h = 180$ and a Langmuir isotherm with parameters $h = 180$, $A = 0.005$ and a diffusion coefficient of $2.10 \cdot 10^{-6}$ were used in parallel.

This experiment allows us to estimate the maximum measurement uncertainties resulting from the simplification of the actual shape of the isotherm (close to Langmuir), with a linear isotherm, at about 25% (Fig. 14). Of course, this is an analysis of a specific case, represented by a set of parameters, and the final scale of uncertainty will be determined by the discrepancy between the shape of the actual and linear isotherm.

4.1. Approximation of measurement data with a numerical model for Langmuir isotherms – the potential of the numerical model

Having measurements of many sorption points that form a sorption isotherm, based on successive sorption kinetics, we can perform extended extraction of parameters with nonlinear sorption isotherm coefficients (e.g. Langmuir). This operation is impossible for a single sorption point. In this case, the optimisation module, which aims to match the process parameters with respect to the recorded course of the experiment, is more complex. Except for the diffusion coefficient, two parameters of the Langmuir isotherm are also subject to fitting. The complexity of the solution space implies difficulties in using typical gradient methods.

The authors searched the solution space using a method similar to simulated annealing. In the initial, wide area of searched ranges, using many stochastic trials, diffusion and Langmuir coefficients, an initial optimum was determined. Then the process was repeated many times, with the new stochastic search area being narrowed around the point of the previous optimum. After meeting the condition of no improvement in the optimised results despite a specified number of trials, the algorithm returned the value of the diffusion coefficient and Langmuir isotherm

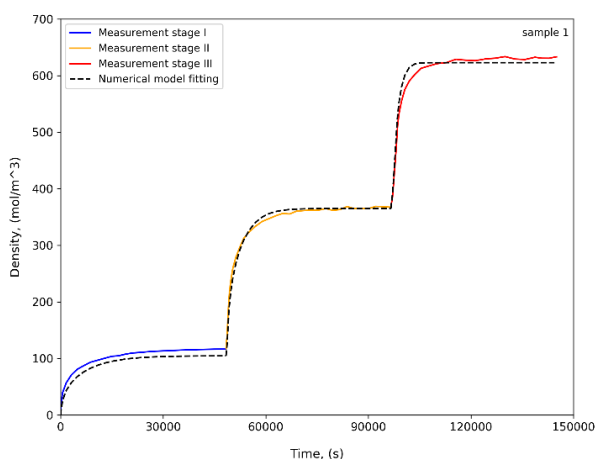


Fig. 15. Approximation of all measurement phases (sample 1) with the numerical model with the Langmuir isotherm

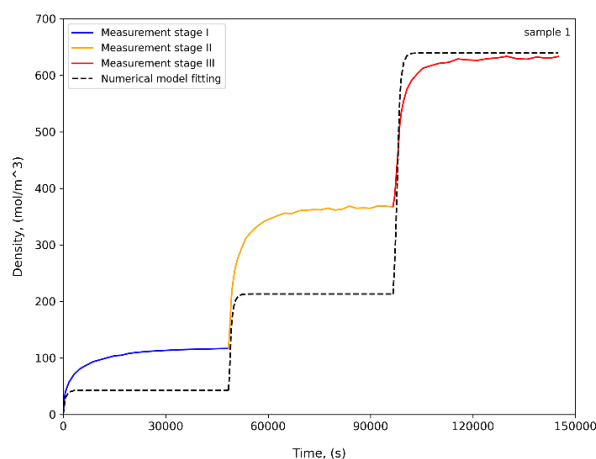


Fig. 16. Approximation of all measurement phases (sample 1) with a numerical model with a linear isotherm

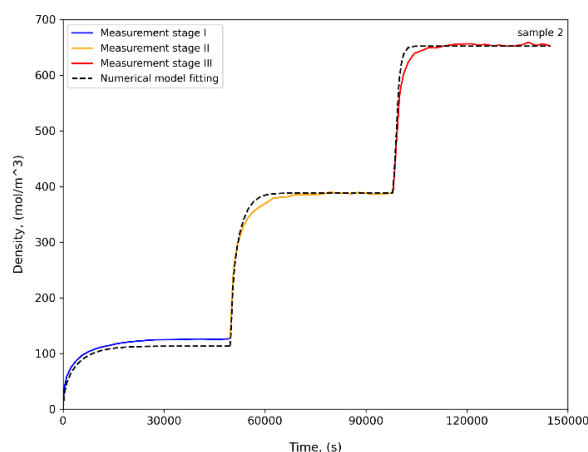


Fig. 17. Approximation of all measurement phases (sample 2) with the numerical model with the Langmuir isotherm

parameters that best fit the measurement data. It should be emphasised that the entire kinetics, for the subsequent pressures tested, is represented by one diffusion coefficient.

The introduction of a numerical model with the implemented Langmuir sorption isotherm allowed for the simultaneous extraction of dynamic parameters (diffusion coefficient) and static parameters (isotherm coefficients). This procedure allowed for the modelling of sorption kinetics for many sorption points (Figs. 15, 17, 19). Without the introduction of the Langmuir isotherm, the extraction of the diffusion coefficient – assuming a constant value based on the linear isotherm for subsequent sorption points – would not have yielded satisfactory results (see Figs. 16, 18, and 20).

If we decide to abandon the Langmuir isotherm (Fig. 21), we cannot treat the diffusion coefficient as a material constant. For individual sorption kinetics, corresponding to subsequent

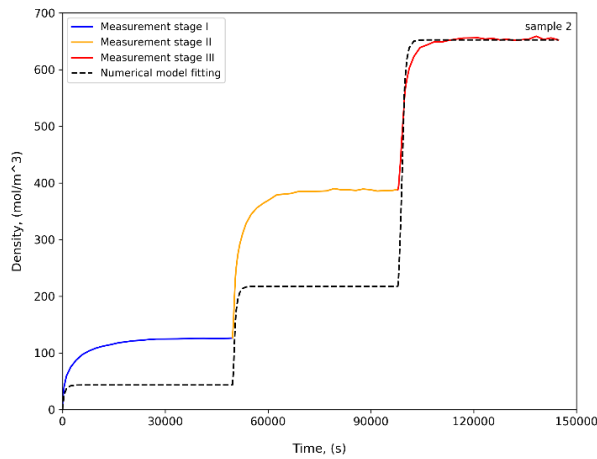


Fig. 18. Approximation of all measurement phases (sample 2) with a numerical model with a linear isotherm

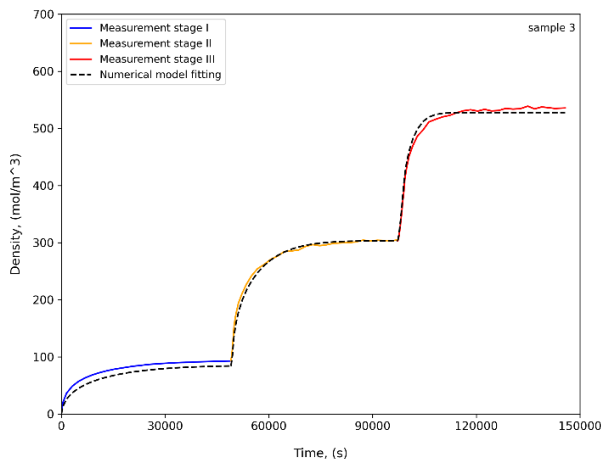


Fig. 19. Approximation of all measurement phases (sample 3) with the numerical model with the Langmuir isotherm

sorption points determined in subsequent, higher sorbate densities, as a result of significant and non-negligible changes in the slope of the linear isotherm, this will result in the extraction of diffusion coefficient values that differ for individual phases of the experiment (Fig. 22).

TABLE 2 presents the values of diffusion coefficients determined for 3 samples, for subsequent stages of determining sorption isotherms at increasing sorbate densities (numerical model with linear sorption isotherm). At the same time, these values were compared with the diffusion coefficient, approximated on the basis of the numerical model with a Langmuir isotherm.

In the presented approach, many research works focusing on the attempt to determine the dependence of the diffusion coefficient value on density (or pressure) are burdened with formal

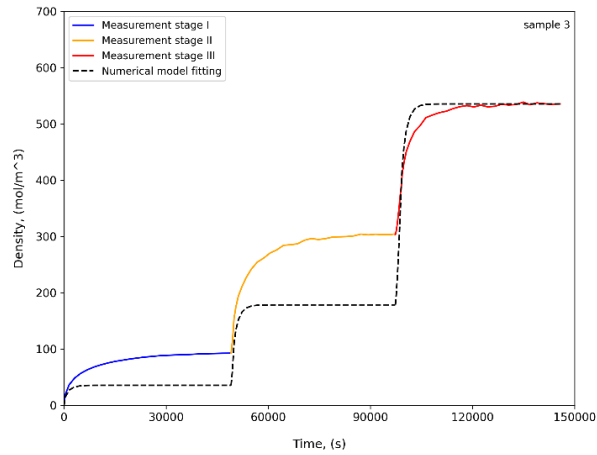


Fig. 20. Approximation of all measurement phases (sample 3) with a numerical model with a linear isotherm

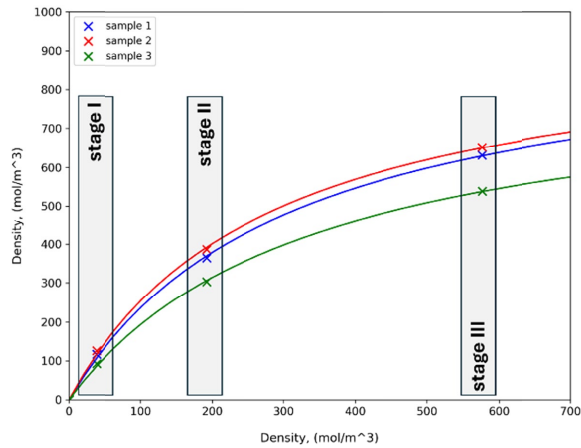


Fig. 21. Langmuir isotherms for tested coal samples with respect to methane

TABLE 2

Approximated diffusion coefficients using a numerical model with a linear isotherm and a numerical model with a Langmuir isotherm

Sample no	Fitting with a numerical model with a linear isotherm, D , (m^2/s)			Fitting with a numerical model with the Langmuir isotherm, D , (m^2/s)
stage	stage I	stage II	stage III	one for all stages
sample 1	5.47e-13	6.32E-13	6.98E-13	5.13E-13
sample 2	6.53e-13	7.80E-13	8.50E-13	6.38E-13
sample 3	3.40e-13	3.96E-13	4.27E-13	2.41E-13

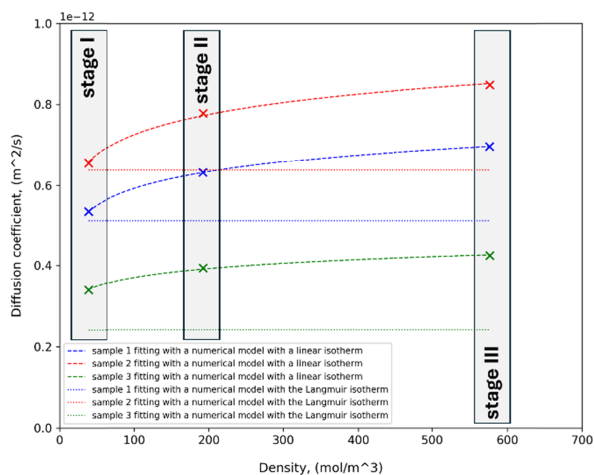


Fig. 22. Variation of the diffusion coefficient as a function of concentration assuming a linear sorption isotherm

errors in their very concept, because the approximation of the measurement at increasing sorbate densities, with a model assuming a linear isotherm, results in the variability of the diffusion coefficient value for subsequent densities, as a result of the deviation of the linear and actual isotherms (Fig. 21).

5. Conclusions and summary

As a result of sorption processes, the sorbent accumulates a certain amount of sorbate. This quantity is a feature of the sorbent-sorbate system and, under established thermodynamic conditions, is defined by the sorption isotherm constructed on the basis of a series of measurement points (sorption capacities). This group of important features determines the potential of the sorbent as a material used to accumulate the desired components (gaseous or liquid). However, the utility of potential sorbents is also shaped by the parameters describing the rate of sorbate accumulation and emission. A sorbent with a large sorption capacity must also provide an effective time response. If the process of filling the sorption capacity lasts unacceptably long, the applicability of the sorbent decreases significantly. The basic parameter characterising the rate of sorbate transport processes with accompanying sorption is the diffusion coefficient. This paper presents an extensive analysis of the phenomenon of sorbate transport and sorption in the porous structure of the sorbent. As a result of simplification, these phenomena are often called sorption kinetics. However, it should be remembered that sorption itself, understood as a change in the number of degrees of freedom of sorbate molecules near the sorbent surface, is almost instantaneous, and all time constants are the effect of the time-consuming transport of sorbate in the complex pore structure of the sorbent. As a result, the analysis concerns the kinetics of gas diffusion coupled with maintaining local momentary sorption equilibria.

Traditionally, the analysis of broadly understood sorption kinetics is based on analytical solutions of Fick's equations, which are known in the literature [19,20]. However, it should be

remembered that the analytical solution is based on a number of assumptions and simplifications. The most important assumption that allowed us to provide an analytical solution is the linearity of the sorption isotherm. The use of a linear isotherm for a certain group of sorbents in a narrow range of sorbate densities may be justified. The linear isotherm for low sorbate densities is often close to the real isotherm, and in this range, we will achieve results similar to the models based on more complex isotherms.

The assumption of isotherm linearity is also helpful during the construction of complex numerical models. It allows for verifying the work of the numerical model based on a comparison with the analytical model. This approach was the first step in the construction of the model used by the authors. After verification, the model was modified by the Langmuir isotherm. The numerical model with a nonlinear sorption isotherm opens up significant possibilities. It also opens a discussion on the idea of the diffusion coefficient as a parameter characterising the sorbate-sorbent system in terms of sorption kinetics. Can we treat this coefficient as a material constant? The article presents the effect of approximating the measured sorption kinetics for several sorbate density values with a numerical model. The approximation of single kinetics, especially for low sorbate densities, with a linear isotherm model is problem-free. However, for several sorption points, when the sorption equilibrium state enters nonlinear regions, approximation with an analytical or numerical model with a linear isotherm is not possible. Approximation of such measurement data with a numerical model with the Langmuir isotherm gives satisfactory results. If we try to approximate measurement data for several sorption capacities individually with a linear isotherm model, we will come to the conclusion that the diffusion coefficient depends on the sorbate density. This is an obvious artefact resulting from the transition to the regions of subsequent slopes of the actual sorption isotherm. In this situation, deviations of the linear isotherm from the actual one are examined, and the variation of the diffusion coefficient as a function of density remains only the effect of using a model with a linear isotherm in problems requiring the use of a more complex relation. If we use a diffusion model with the Langmuir isotherm, or another one adequate to the nature of the sorbent, we can treat the diffusion coefficient as a material constant.

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