Nonlinear and Linear Equation of Gas Diffusion in Coal—Theory and Applications

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Abstract: The authors derived the analytical solution to diffusion equations. The solution requires linearization of diffusion equations, as well as developing the obtained expression into a series. In particular, the result of the first procedure is highly deviated from the exact solution. The authors conducted a sorption experiment and then, in relation to the registered kinetics of the diffusion of CO$_2$ inside hard coal grains, approximated the linear solution and the numerical nonlinear solution by means of the least squares method. As confirmed by the lower value of the sum of deviation squares, it can be clearly demonstrated that the nonlinear equation represents the actual measurement more accurately.

Keywords: nonlinear diffusion equation; linear diffusion equation; effective diffusion coefficient; kinetics of CO$_2$ diffusion

1. Introduction

Research connected to the evaluation of the sorption properties of porous sorbents usually concerns steady states, during which single points of sorption equilibriums or sorption isotherms are established. There are, however, a number of problems that call for taking into account the time factor, i.e., analyses of accumulation kinetics or the emission of a sorbate from a sorbent. The usage of the term ‘accumulation kinetics’, or the emission of a sorbate from a sorbent, instead of the term ‘sorption/desorption kinetics’, is here perfectly justified. In the case of the sorption process, understood as reducing the number of degrees of freedom of the molecules of a gaseous sorbate near the sorbent surface [1–4], it may be assumed that a process defined in such a way occurs almost instantaneously [5]. All the temporal relationships are connected with the transportation of the molecules of a gaseous sorbate within the grains of a sorbent [6,7]. The amount of sorbed gas molecules depends, in turn, on the parameters of the sorption process and the degree of development of the pore space of grains [8–15].

The gas transport phenomena taking place within the porous structure of the sorbent can be considered as (i) seepage process—driven by a pressure gradient and occurring in the area of mesopores, macropores, and fractures, and (ii) diffusion process—driven by a concentration gradient and occurring in the micropores and ultramicropores [16]. The most commonly used equations describing both processes are Darcy’s law [17] and Fick’s law [18], respectively. Many models have been developed to describe gas transport processes within the pore structure of coal, which are based on Darcy’s and Fick’s laws [19–26]. Because more than 90% of the pores in hard coal are less than 1 nm in diameter, coal is considered to be an ultramicroporous rock [27], and diffusion is the dominant transport process within coal grains.

This paper presents a linear and nonlinear diffusion equation, along with the respective solutions of the two—an analytical and differential one. Additionally, an experiment that involved registering the temporal course of CO$_2$ sorption on a granular hard coal
sample was conducted, and the obtained results were used in the process of extrapolation with models based on the linear and non-linear diffusion equation.

The paper systematizes the theoretical knowledge of the diffusion of a gaseous sorbate in a porous sorbent [28]. It presents an original line of reasoning which leads—from the law of mass conservation and motion equations, through linearization of the diffusion equation—to an analytical solution in the form of a series development, convergent with the solution proposed by Crank and Timofiejew [29,30]. Additionally, a numerical solution of the nonlinear equation was provided. An experiment was conducted, during which the kinetics of carbon dioxide diffusion within hard coal grains was registered. Theoretical data—both from the analytical and numerical solution—was matched with the measurement data. These issues are very important, as on the basis of the phenomenon’s physical models, parameters describing the course of the investigated processes are developed [31]. The effective diffusion coefficient proposed by Crank [29], widely applied in the extraction industry, is one such parameter.

2. Assumptions of the Gas Diffusion Equation in a Granular Sorbent

In order to provide a theoretical description of the emission of a gaseous sorbate from a grain of a sorbent, we shall look into the equation of the diffusion process with its source in desorption of a sorbate bound with a sorbent. We shall assume that the sorbent grains have a shape of a sphere, whose radius is $r_0$. Inside a grain, a gaseous sorbate in two states occurs: pore-located free gas and sorbed gas [32–35].

Let us denote the mass of free gas as $m_g$, the mass of sorbed gas as $m_z$, and the grain volume as $V_w$. The porosity of the grain, understood as the relationship of the pores’ volume to the total grain volume, equals $\psi$. For these denotations, the densities of free gas, $\rho_g$, and sorbed gas, $\rho_z$, shall be expressed with the following formulas:

$$\rho_g = \frac{m_g}{\psi \cdot V_w} \quad \rho_z = \frac{m_z}{V_w}$$  \hspace{1cm} (1)

where:
- $\rho_g$ is the density of free gas (kg/m$^3$);
- $\rho_z$ is the density of sorbed gas (kg/m$^3$);
- $m_g$ is the mass of free gas (kg);
- $m_z$ is the mass of sorbed gas (kg);
- $V_w$ is the grain volume (m$^3$);
- $\psi$ is the porosity (-).

Generally, in the case of a non-stationary process, densities $\rho_g$ and $\rho_z$ are functions of time and a radius, $\rho(r, t)$. Both the theoretical and experimental analyses [5] demonstrate that the process of sorption proper, understood as the transition of gas molecules from the bonded state to the free state, is almost instantaneous. Therefore, let us assume that sorption has no impact on the speed with which gas penetrates the pore structure of a sorbent. It also needs to be assumed that the process of gas emission from a grain is isothermal in its nature. Free gas is treated as ideal gas, and thus the relationship between pressure and gas density is expressed as follows:

$$p = C \cdot \rho_g$$  \hspace{1cm} (2)

where:
- $p$ is the gas pressure (Pa);
- $C = \frac{R \cdot T}{M}$ (m$^2$/s$^2$);
- $R$ is the universal gas constant (J/(mol·K));
- $T$ is the temperature (K);
- $M$ is the molecular mass of gas (kg/mol).
The next assumption concerns the sorption isotherm. In the case of the processes occurring under low sorbate pressure, it might be assumed that the sorption isotherm is linear and that it can be described by means of Henry’s law [36]:

$$\rho_z = H \cdot p = H \cdot C \cdot \rho_s$$

(3)

where:

$H$ is Henry’s coefficient (s$^2$/m$^2$).

The relationship between the density of sorbed gas, $\rho_z$, and the amount of sorbed gas, $a_m$, expressed in cubic meters of gas per one kilogram of sorbent and adapted via calculation to the standard conditions of pressure and temperature, is demonstrated by the following formula:

$$\rho_z = \frac{m_w \cdot M \cdot p_N}{R \cdot T_N \cdot V_w} a_m = \frac{\rho_w \cdot M \cdot p_N}{R \cdot T_N} a_m = S \cdot a_m$$

(4)

where:

$m_w$ is the grain mass (kg);

$T_N$ is the temperature under standard conditions (K);

$p_N$ is the pressure under standard conditions (Pa);

$\rho_w$ is the coal density $m_w V_w$ (kg/m$^3$);

$a_m$ is the amount of sorbed gas (m$^3$/kg);

$S = \frac{\rho_w \cdot M \cdot p_N}{R \cdot T_N}$ is the constant value (kg$^2$/m$^6$).

3. Gas Diffusion Equation in Sorbent Grains

The differential form of the law of mass conservation, applied to a grain of a sorbent in which gas in a free and sorbed form occurs, is expressed as follows [29]:

$$\frac{\partial (\rho_z + \psi \rho_s)}{\partial t} + \text{div} \left( \rho_g \cdot \vec{v} \right) = 0$$

(5)

where:

$\vec{v}$ is the diffusion process rate (m/s).

The equation of gas motion is expressed by Darcy’s law [17]:

$$\vec{v} = -\frac{k}{\mu} \text{grad} p$$

(6)

where:

$k$ is the permeability coefficient (m$^2$);

$\mu$ is the gas dynamic viscosity (N·s/m$^2$).

It can be assumed that the permeability coefficient, $k$, is constant and independent of both the radius and time. Once the motion Equation (6) is substituted into the continuity equation—while taking into account the gas state Equation (2) and linear sorption isotherm Equation (3) and introducing the dimensionless gas density, $\xi (r, t) = \frac{\rho_g (r, t)}{\rho_{\text{max}}}$ (the maximum, initial gas density)—we obtain the following formula:

$$\frac{\partial \xi}{\partial t} = D \cdot \nabla^2 \xi^2$$

(7)

where:

$$D = \frac{k \cdot C \cdot \rho_{\text{max}}}{2 (H \cdot C + \psi)}$$

is the diffusion coefficient (m$^2$/s).
Equation (7) is analyzed in a spherical coordinate system. According to the conditions of the experiment, the equation should be solved for the following boundary-initial conditions:

\[
\begin{align*}
\rho_g(r,0) &= \rho_{\text{max}}, \\
\rho_g(r_0,t) &= 0, \\
\frac{\partial \rho_g}{\partial r} &= 0, \\
\xi(r_0,t) &= 0,
\end{align*}
\]

(8)

The first condition means that, at the initial moment, the density of free gas inside a grain equals \(\rho_{\text{max}} = \frac{p_0}{C}\), where \(p_0\) is the pressure of a gaseous sorbate saturating a porous sorbent. The second condition means that, outside a grain, gas density equals zero. The third condition concerns the symmetry of the distribution of free gas density in relation to the center of a grain of a sorbent.

Equation (7), with its boundary-initial conditions (8), can be solved in a numerical way by applying the finite element method (FEM). A condition for solving the equation is knowledge of the diffusion coefficient, \(D\). The density of gas in a grain of a sorbent may change to a significant degree, which is why the analyzed equation is nonlinear. However, if we investigate the final or the initial stadium of the process kinetics, we shall see that the gas density within a grain changes to a much lesser extent. Therefore, in these particular stages of the process, the diffusion equation can assume the linear form:

\[
\xi = \xi_0 + \xi'
\]

(9)

where:

\(\xi_0\) is the density of gas after the time period in which 80% of the sorbed gas was released.

After substituting Equation (9) into Equation (7), while neglecting the small quantities of the second order, \((\xi')^2\), we shall obtain the following formula:

\[
\frac{\partial \xi'}{\partial t} = 2 \cdot D \cdot \xi_0 \cdot \nabla^2 \xi'
\]

(10)

Equation (10) is the linear diffusion equation, whose solution, under condition (8), is expressed by the series given below [37]:

\[
\xi' = 1 - \frac{2 \cdot r_0}{\pi \cdot r} \cdot \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \cdot \sin \left( \frac{n \cdot \pi \cdot r}{r_0} \right) \cdot \exp \left( -\frac{n^2 \cdot \pi^2 \cdot D'}{r_0^2} \cdot t \right),
\]

(11)

where:

\(D' = 2 \cdot D \cdot \xi_0\) (m²/s).

In the course of the experiment, it is possible to determine the amount of gas released from a grain—thus, we are interested in the average gas density inside a grain. In order to establish it, we shall calculate a density integral over a grain radius [38]:

\[
\gamma = \frac{3}{r_0^2} \int_0^{r_0} r^2 \cdot \xi' (r,t) dr
\]

(12)

where:

\(\gamma\) is the average gas density inside a grain.

Following the integration of Function (11) according to formula (12), we shall receive:

\[
\gamma = 1 - \frac{6}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp \left( -\frac{n^2 \cdot \pi^2 \cdot D'}{r_0^2} \cdot t \right)
\]

(13)
Function (13) can be approximated with its asymptotic expansions for large and small time values. After a sufficiently long amount of time passes in the final desorption stage, function \( \gamma \) can be approximated by means of the following formula:

\[
\gamma_\infty = 1 - \frac{6}{\pi^2} \cdot \exp \left( -\frac{\pi^2 \cdot D' \cdot t}{r_0^2} \right)
\]  

(14)

where:

\( \gamma_\infty \) is the amount of gas released at the final desorption stage.

For the initial moments of the desorption process, in turn, the function approximation is expressed by the following formula:

\[
\gamma_m = \frac{6}{r_0} \sqrt{\frac{D' \cdot t}{\pi}}
\]  

(15)

where:

\( \gamma_m \) is the amount of gas released at the initial desorption stage.

Figure 1 presents an exact, radius-averaged solution to Equation (7) (formula (13)) and its asymptotic approximations (14) and (15).

Figure 1. Comparison of approximate solutions (Equations (14) and (15)) of the linear diffusion equation with the exact solution (Equation (13)).

As can be seen, when the relative amount of the gas released from a sorbent grain reaches the value \( \gamma = 0.8 \), the approximate solution of the diffusion coefficient is identical with the exact solution. Let us denote as \( t_{0.8} \), the time after which the amount of gas being released will come to 0.8 of the maximum value. Using formula (14), we can calculate the effective diffusion coefficient \( D'_\infty \):

\[
D'_\infty = -\frac{r_0^2}{\pi^2} \cdot \ln \frac{0.2 \cdot \pi^2}{6} = 0.113 \frac{r_0^2}{t_{0.8}}
\]  

(16)
Similarly, comparing the exact solution with the approximation for the initial desorption stadium, we can see that the former corresponds to the latter up to the value \( \gamma = 0.2 \). Therefore, on the basis of formula (15), we can determine the following:

\[
D'_m = \left( \frac{0.2}{6} \right)^2 \cdot \frac{r_0^2 \cdot \pi}{t_{0.2}} = 0.21 \cdot \frac{r_0^2}{t_{0.2}}
\]  

(17)

where:

\( t_{0.2} \) is the time after which the amount of gas being released reaches 0.2 of the maximum value (s).

Analyzing the exact solution (13), one can demonstrate that, for \( \gamma = 0.5 \), the value of the effective diffusion coefficient will be inversely proportional to the half-time, \( t_{0.5} \), according to the following relationship:

\[
D'_{0.5} = 0.3016 \cdot \frac{r_0^2}{\pi^2 \cdot t_{0.5}}
\]  

(18)

where:

\( t_{0.5} \)—is the time after which the amount of gas being released reaches 0.5 of the maximum value [s].

4. Numerical Solution of the Nonlinear Diffusion Equation

In order to solve the nonlinear diffusion equation, the numerical finite difference method was applied. By deriving the Laplace operator to spherical coordinates—while taking into account the angular symmetry—and by making the substitution \( \eta = \xi^2 \), we shall receive the following formula:

\[
\frac{\partial \eta}{\partial t} = 2 \sqrt{\eta} \cdot D \cdot \left( \frac{\partial^2 \eta}{\partial r^2} + \frac{\partial \eta}{\partial r} \right)
\]  

(19)

Below, the boundary-initial values under which Equation (19) will be solved are specified:

\[
\begin{align*}
\eta(r, 0) &= 1 \quad \rightarrow \quad 0 \leq r \leq r_0 \\
\eta(r_0, t) &= 0 \quad \rightarrow \quad t \geq 0 \\
\frac{\partial \eta}{\partial r} &= 0 \quad \rightarrow \quad t \geq 0, r = 0.
\end{align*}
\]  

(20)

The differential scheme for Equation (19) shall look as follows:

\[
\eta_{i,j+1} = \left( 1 - 2 \cdot \chi \sqrt{\eta_{i,j}} - \frac{2 \chi}{t} \right) \cdot \eta_{i,j} + \left( \chi \sqrt{\eta_{i,j}} + \frac{2 \chi}{t} \right) \cdot \eta_{i+1,j} + \chi \sqrt{\eta_{i,j}} \cdot \eta_{i-1,j}
\]  

(21)

where:

\( \chi = \frac{D_k \cdot k_t}{h_r^2} \) is the parameter related to the stability of the solution;

\( h_r = \frac{r_0}{n} \) is the step of the spatial grid (m);

\( k_t = \frac{\chi \cdot h_r^2}{D} \) is the step of the temporal grid (s).

The stability of the solution to Equation (21) depends on parameter \( \chi \). For the parabolic equation, a stable (oscillation-free) solution for condition \( \chi < 0.5 \) is obtained. In the case of the nonlinear equation, there is no definite value of parameter \( \chi \), which would guarantee the stability of the solution.

The calculation scheme involves using the known density of gas in a particular time step in a whole coal grain in order to calculate the density in the next step. For the sake of the calculations, it was assumed that \( \chi = 0.4 \). For such parameter \( \chi \), the solution of the diffusion equation is monotonic and compatible with the course of the curves in the experiment.
The grain radius was divided into 24 parts \((n = 24)\). The initial value of the relative density distribution is equal to 1. In each temporal step, the distribution of density inside a grain was calculated and then averaged:

\[
\gamma = \frac{3}{h^3} \cdot \frac{1}{r^3_0} \sum_{i=1}^{n} \sqrt{\gamma_i} \cdot i^2
\]  

(22)

The diagram of the spherical grain division adopted for the calculation of changes in gas density within its individual parts during gas emission is shown in Figure 2.

![Diagram of spherical grain division](image)

Figure 2. Scheme of the spherical grain division adopted for the calculation of gas density changes within its individual parts during gas emission.

5. Comparison of the Measurement Results with the Solution of the Nonlinear Diffusion Coefficient

For the sake of the experimental research, the grain samples of hard coal of four different fractions were used [23]. The coal came from the “Thorez” coal mine in the Lower-Silesian Coal Basin, Poland [39]. The research was carried out by means of the volumetric method [4,40], at a stabilized temperature of 30 °C. The sorbate was carbon dioxide \((\text{CO}_2)\), with which the coal sorbent was saturated for 24 h at a stabilized pressure of 0.25 MPa. The saturation process was preceded by outgassing the coal for 24 h by means of a vacuum pump, under a temperature of 80 °C. For the chosen grain fraction, these time values proved sufficient to obtain sorption equilibriums.

Table 1 shows the results of \(\text{CO}_2\) desorption measurements from coal samples of different grain sizes after initial saturation of these samples to a pressure of 0.25 MPa and emission of the gas to the vacuum. The amount of released gas was determined by the volumetric method, based on the measurement of pressure changes in the container to which the gas was released from the sample. Time dependencies of sorption changes \((a(t))\) were determined from the Clapeyron equation.

| Grain Size (mm) | Equivalent Grain Size \(r_0\) (mm) | Sorption Capacity \(a_m\) (cm\(^3\)/g) | \(t_{0.2}\) (s) | \(t_{0.8}\) (s) | \(D_m' \cdot 10^{-13}\) (m\(^2\)/s) | \(D_\infty' \cdot 10^{-13}\) (m\(^2\)/s) |
|----------------|-----------------------------------|-------------------------------------|----------------|----------------|-----------------------------------|---------------------------------|
| 25–32          | 14.1                              | 9.81                                | 0.33           | 65             | 16.5                              | 2.7                            |
| 63–72          | 33.6                              | 9.95                                | 1.08           | 340            | 32.1                              | 2.9                            |
| 90–100         | 47.4                              | 9.90                                | 3.03           | 964            | 23.3                              | 2.4                            |
| 200–250        | 111.6                             | 9.78                                | 27.7           | 4520           | 12.6                              | 2.5                            |
For the model calculations, for each grain size range, an equivalent grain size ($r_0$) was assumed, which was calculated from the formula:

$$r_0 = \frac{1}{2} \sqrt[3]{\frac{2 \cdot d_1^2 \cdot d_2^2}{d_1 + d_2}}$$  \hspace{1cm} (23)

where: $d_1$ and $d_2$ are the grain size limits of the size of the analyzed grain fraction.

By determining the times, $t_{0.2}$ and $t_{0.8}$, from the registered courses, the diffusion coefficients, $D'_m$ and $D'_\infty$, were calculated from Equations (16) and (17). Comparing the values of these coefficients, it can be seen that, in the initial stage, the process of gas emission from the grains of coal samples is much faster, and the $D'_m$ values are about an order of magnitude higher than $D'_\infty$. Therefore, courses that are described by nonlinear diffusion, Equation (10), are difficult to characterize by one parameter that determines the gas emission rate.

The results of the experiment were compared with the model based on the exact solution of the linear diffusion equation and the numerical solution of the nonlinear diffusion equation (Figure 3). According to expectations, linearization of the diffusion equation results in a poorer representation of the experimental course, which is confirmed by a substantially bigger number of deviation squares. The values of the diffusion coefficients differ by more than two times.

Figure 3. Comparison of the linear and nonlinear solution of the diffusion equation with the experimental result—example for a sample of hard coal with a grain size of 90–100 mm.

Figure 4 shows a comparison of the experimental results with the model results described by the nonlinear diffusion equation, obtained for four different grain classes. The initial CO$_2$ saturation pressures were 0.25 MP, and then the gas emission into the vacuum was recorded for 100 min. Depending on the grain size, the asymptotic value of the ratio of the amount of gas released to the total amount of gas sorbed in the sample was reached after different periods of time. With increasing grain size, the time to reach sorption equilibrium increases. The presented comparison of the measurement results with the model results described by the nonlinear diffusion equation confirmed the consistency of the results.
Figure 4. Comparison of the nonlinear solution of the diffusion equation with the experimental results obtained on samples of different grain sizes.

6. Conclusions

In the case of porous sorbents, the kinetics of the sorption processes is a question of both the transportation of molecules within the pore structure of the material and the proper sorption—being, as a matter of fact, the reduction in the number of the degrees of freedom of the sorbate molecules. The other of the two processes, as the theory and only a few experiments demonstrate, is almost instantaneous in its nature. In a porous sorbent, the diffusion coefficient can be determined—a parameter describing the kinetics of accumulation or emission of a gaseous sorbate.

The authors derived the analytical solution of the diffusion equation. The solution requires linearization of the diffusion equations, as well as developing the obtained expression into a series. In particular, the first procedure yields deviations from the exact solution. The authors conducted a desorption experiment, and then—in relation to the registered kinetics of the diffusion of CO$_2$ inside hard coal grains—approximated the linear solution and the numerical nonlinear solution by means of the least squares method. As confirmed by the lower value of the sum of deviation squares, it can be clearly demonstrated that the nonlinear equation represents the actual measurement more accurately.

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