



# Modeling and experiments for transient diffusion coefficients in the desorption of methane through coal powders



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## ABSTRACT

Diffusion is widely thought to be the key factor that controls the desorption of gas through porous media. However, the classical diffusion model with a constant Fick diffusion coefficient is inadequate for describing desorption from coal over the entire timescale. In this study, a new model to describe the time-dependent diffusion coefficients during desorption was developed. Experiments including proximate analyses, isothermal adsorptions, mercury intrusions, N<sub>2</sub> adsorptions and methane desorptions were conducted to verify its validity. The results demonstrated that the Fick diffusion coefficients decreased over the desorption period first sharply and then slowly. By introducing the time-dependent relationship into the general unipore model, we obtained a unipore diffusion model with  $D(t)$  (UDMD), which had a better degree of fit with the laboratory desorption than that of the original. Moreover, the simplification for the UDMD was acquired for engineering applications.

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## 1. Introduction

Diffusion has long been a heated scientific topic when trying to explain the migration of gas thorough porous media, such as catalysts or coal. In the area of natural gas engineering, a suitable description is of great importance to the prediction of methane content, the explanation of the sorption process, the evaluation of the greenhouse effect and the prevention of methane dynamic hazards [44,6,20,21,23,43,50,35,53]. The classical Fick's diffusion law originally took diffusion as the movement of a substance down a concentration gradient. In that equation, the diffusion coefficient is defined as the diffusing mass per unit time through a unit area of a section along the diffusing direction when there is a unit concentration gradient. Crank [10] stated that the diffusion coefficient is a variable parameter that is affected by the concentration  $c$ , position  $x$  and time  $t$ . In contrast, more researchers have regarded it as a

constant due to the limits of experiments and the difficulty of acquiring mathematical solutions. They preferred using a fitting method to obtain the apparent diffusion coefficient, especially when trying to apply Fick's law to porous media, such as coal or clay [27,6,1,9,13,18,38].

Crank [10] first provided detailed mathematical solutions to the diffusion equations through media of various shapes, such as sheets, cylinders and spheres with different boundaries. People usually call that model of spherical diffusion as the unipore model because it assumes diffusion through homogeneous unipore media. Nevertheless, the solutions to the unipore model are mostly written as infinite series, which are not easily applied in engineering; other scientists have therefore attempted to simplify them. A famous simplification is called the  $\sqrt{t}$  model for small times [30]. It is used to obtain diffusion coefficients or to predict the loss content of gas when drilling. The effect of fitting the  $\sqrt{t}$  model is also regarded as an index to evaluate whether the diffusion is controlled by inner pores or the outer surface [19]. There are several other empirical models that have been applied to methane migration, including Yang's model [46] and Nie's model [31]. All of the models above are simplifications or approximations of Crank's solution and are therefore unipore models (Fig. 1).

*Abbreviations:* UDM, unipore diffusion model; UDMD, unipore diffusion model with  $D(t)$ ; UDMS, unipore diffusion model simplification; UDMS, unipore diffusion model with  $D(t)$  simplification; NMR, Nuclear Magnetic Resonance.

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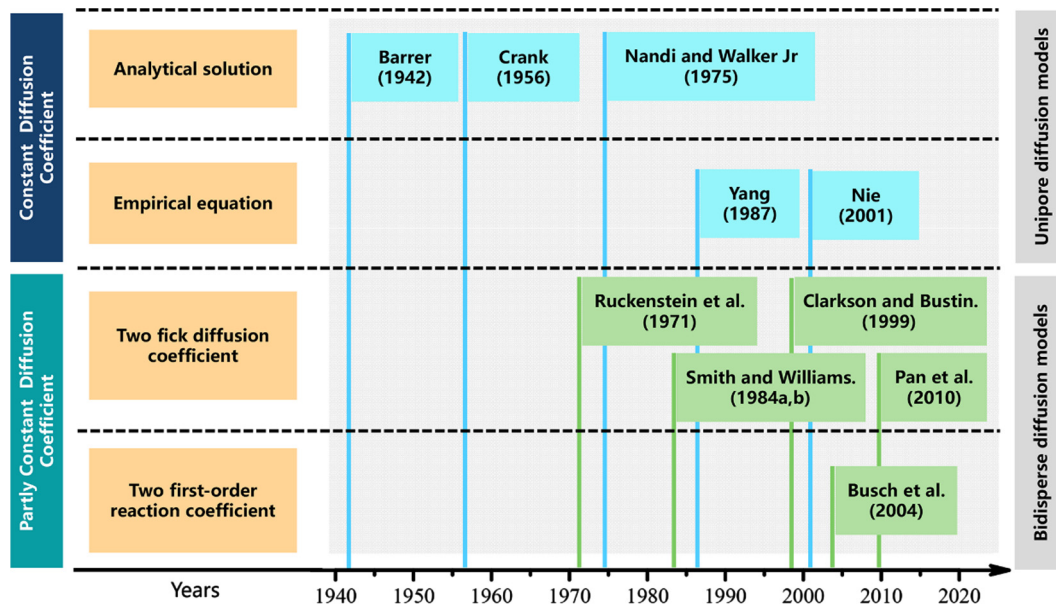


Fig. 1. Frequently used methane sorption models in coal.

However, real porous media are not homogeneous, and the unipore model fails to obtain good fits with desorption data over the entire timescale of desorption [9,38]. It is possible to solve the problem of poor fits by assuming that the diffusion coefficient is variable. The bidisperse model, which is widely used as the unipore model in the gas diffusion area, can be regarded as the first try in using a variable diffusion coefficient [7,14,37]. Although there are two different coefficients for macropores and micropores, the bidisperse model fails to escape the assumption of constant diffusion coefficients in certain pore systems. Zhang [49] once noted that it is impossible, without simplifications, to acquire accurate analytical solutions to Fick's law when the diffusion coefficient depends on the concentration  $c$  and position  $x$ . However, for time  $t$ , an analytical solution is possible. Therefore, a solution can be more feasibly obtained from the perspective of time  $t$  if we want to obtain a variable diffusion coefficient.

With respect to the time-dependent diffusion coefficient  $D(t)$ , most research has focused on the self-diffusion coefficient  $D_{\text{self}}$  when the concentration gradient is zero [4,19,24,29,40]. A single molecule, diffusing through porous media, will encounter different forces from the pore wall. When under transport, it will lose its initial kinetic energy, which leads to a decreasing self-diffusion coefficient. Regarding the time-dependent Fick diffusion coefficient, many scholars have focused on the explanation of how the Fick diffusion coefficients change with time and the measurement of the time-dependent Fick diffusion coefficients. Gregory Staib et al. [39] concluded that for different stages, the diffusion coefficient will exhibit different dependence with pressure or concentration. A pressure dependence is observed for the fast diffusion coefficient, while the slow diffusion coefficient is more consistent with a concentration dependence. They also suggested to use a Fickian diffusion-relaxation model, as developed by Berens and Hopfenberg [3] based on the 'stretched exponential' model [12], to fit the desorption data. Time-dependent Fick diffusion coefficients can be obtained via the semi-empirical method from general desorption experiments [21,27,22,48]. Li et al. [22] and Yuan [48] tried to use an empirical model to fit the time-dependent diffusion coefficient, but this empirical form is not strongly convincing. Therefore, it is vital to find an appropriate mathematical model to describe this time-dependent diffusion phenomenon.

## 2. Mathematical model

### 2.1. Model assumption

Assumptions need to be made during desorption. The process of methane molecules moving from the adsorbed state to ambient air can be divided into three constituent parts: desorption from the pore surface, diffusion through pore tunnels and breaking through the gas film surrounding the particle. Among those parts, diffusion is the slowest and thus controls the rate of the entire desorption process. Einstein and Stokes once analyzed the force of a spherical particle of radius  $r$  through laminar flow and obtained the Stokes-Einstein equation to describe the diffusion coefficient in continuous fluid media [42]. Analogously, diffusion coefficients can be obtained from flow force analysis. Lowell et al. [25] stated that if the pore shapes are highly irregular or consist of a mixture of regular geometries, or in the absence of specific knowledge of the pore geometry, the assumption of cylindrical pores is usually made. Thus, transportation in methane sorption can be supposed to occur through cylindrical tunnels of radius  $R$ , as shown in Fig. 2. The assumptions are as follows:

- I. The pressure difference between the two ends of a pore tunnel remains constant during methane sorption. This is because the concentrations of the sphere center and the surface are assumed to be constant in the classical unipore and bidisperse diffusion models [10]. Moreover, if the concentrations are inconstant, the boundary conditions of Fick's diffusion model will be changed and the analytical solution to that becomes difficult.
- II. The temperature and dynamic viscosity of the methane remain constant. The gas viscosity is only influenced by the temperature; thus, it will not change in a constant-temperature system.
- III. The adsorbed gas becomes free gas instantaneously. Adsorption or desorption process is extremely fast compared to diffusion [51]. Thus, the desorption time from the pore wall is ignored and all desorbed gas are assumed to become free gas when desorption begins, following the real gas equations.
- IV. Only the horizontal forces along the tunnel are considered.

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