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Adsorption kinetics and diffusion modeling of CH_4 and CO_2 in Indian shales

Sneha Rani, Basanta K. Prusty*, Samir K. Pal

Department of Mining Engineering, Indian Institute of Technology, Kharagpur 721302, India

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ABSTRACT

The concept of increased gas (methane) recovery with simultaneous CO_2 sequestration in unconventional reservoirs like gas shales has been studied in the past few years. Diffusion is the main transport mechanism in shale gas reservoir. Understanding the methane and CO_2 diffusion properties of shales and its modeling is important for planning successful methane recovery and CO_2 sequestration in these reservoirs. Methane and CO_2 adsorption kinetic studies were carried out at four different pressure steps (in the range of 3.5–8.9 MPa for CH_4 and 2–6 MPa for CO_2) to investigate their diffusion behavior on two shale samples (Pakur and Salanpur) from Damodar Valley Basin, India. The sorption kinetic data was modeled using unipore model and modified unipore model (MM). The unipore model is giving good match with experimental sorption kinetics data up to a fractional uptake of 62–92% for methane and 62–88% for CO_2. The MM model is giving very good match up to the fractional uptake of 78–99% for methane and 77–98% for CO_2. It was observed that the MM model is giving better fit than that of unipore model for both gases for the entire pressure range. Thus it can be suggested that MM model is a better model to represent the diffusion of methane and CO_2 in shales.

1. Introduction

Anthropogenic emission of greenhouse gases particularly, CO_2 is believed to be responsible for the global climate change. Carbon sequestration has been identified as one of the technological alternatives for reducing CO_2 emission from the atmosphere. Depleted oil reservoirs, saline aquifers and gas-hydrate reservoirs are some of the potential sites for carbon sequestration. The unconventional reserves such as depleted gas shales can also provide a huge sink to sequester CO_2 [1]. Disposal of CO_2 in coal/shale formations may help in achieving the twin objectives of sequestration of the greenhouse gas and enhanced gas recovery (EGR) specifically methane from the gas shale formations. Flow and storage of CO_2 in gas shale seems to be very promising because of the expected economic benefits due to the associated methane production [2]. To optimize this process it is necessary to understand in detail the storage mechanism and flow properties of the shale rock formation.

Gas transport in shales can be explained by dual- or triple-porosity models [3,4]. King et al. [5] states that shale reservoir has a dual-porosity behavior, and is composed of primary porosity and secondary porosity system. The micropores in the matrix of shales constitute the primary-porosity system. The secondary-porosity system consists of cleats and other natural fractures (macropores). The flow of gas in shale reservoirs takes place mainly due to three mechanisms, i.e. desorption, diffusion and viscous flow [6,7]. Depending on the characteristics of the reservoir and gas type, these three mechanisms control the flow. The gas flow in primary- and secondary-porosity system is usually controlled by Fick's law of diffusion and Darcy's law respectively.

The knowledge of gas transport properties of shales is important for successful methane recovery and CO_2 sequestration in shale gas reservoirs. Transport of gas in shale occurs in two stages. In the first phase, diffusion is faster within macropores where molecular diffusion occurs which is controlled by Fickian diffusion. In the second phase, slower diffusion occurs in micropores, i.e. dominated by Knudsen diffusion, where molecular and pore wall collision dominates [8]. The internal surface area of micropores holds a significant part in shale matrix. Although micropore diffusion is considered a single process, it is usually a combination of three types of diffusion. These are namely Knudsen diffusion (where molecule–wall collisions dominate), surface diffusion (transport through physically adsorbed layer) and bulk diffusion (molecule–molecule collisions dominate) [9]. Diffusion is one of the main mechanisms of transport of gas in a shale gas formation that controls the rate of recovery of gas from the gas shale reservoir [10]. The rate of flow of gas from the matrix (micro- and meso-pores) to the fractures (macropores) in shale gas reservoirs is controlled by diffusion. Some of the previous studies, suggest that pore structure has important role in storage and transport of gas in the shale matrix [11,12]. Hence the study of gas transport in shale is important for understanding the gas flow in a shale-gas system.

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* Corresponding author.
E-mail address: bkprusty@mining.iitkgp.ernet.in (B.K. Prusty).

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1.1. Adsorption kinetics and diffusion modeling

Literature on adsorption kinetics of methane and CO_2 on shales are limited. However, numerous studies have been conducted on diffusion and adsorption kinetics of methane and CO_2 on coals and reported in the literature. Considering that some aspect of storage and transport mechanisms in shales and coals are similar, the studies on coals are relevant and discussed below.

Sevenster [13] reviewed the gas flow studies on coal and suggested that unipore model based on the Fick's second law of diffusion was the mostly widely used approach for modeling diffusion in coal. Nandi and Walker [14] conducted experiments on diffusion of methane in three coal samples of varying ranks from USA at pressures up to 2.76 MPa. It was reported that effective diffusivity increased with rise in methane concentration and decreased with particle size of the measured coals. Smith and Williams [15] investigated the applicability of methane adsorption rate data of Fruitland coal samples on unipore and bidisperse diffusion models. It was observed that unipore model gave good fitting to the experimental data for only the initial time range (when fractional uptake is less than 0.5). The bidisperse model however, gave good fitting to the experimental data for the entire time range. Crosdale et al. [16] conducted desorption rate measurements on selected bright and dull coal samples from Bowen Basin, Australia and the results were analyzed using unipore and bidisperse pore-diffusion models. It was reported that the bright, vitrinite-rich coals having highly microporous structure had the slowest desorption rates. It was suggested that faster desorption in bright coals was due to the development of extensive fracture systems. Clarkson and Bustin [17] studied the effect of coal composition, pore structure, and gas pressure upon methane and CO_2 transport in Cretaceous Gates Formation coal. It was stated that coal matrix gas transport models, which assume a homogeneous unimodal pore structure and linear adsorption isotherms, were unable to model adsorption kinetics in all types of coal. A new numerical model was proposed that assumed bimodal pore structure and non-linear isotherm. It was observed that the new numerical model which assumed non-linear adsorption had larger diffusivities compared to that obtained from analytical models for pore diffusion. The CO_2 diffusivities were higher than the methane diffusivities for the studied coal samples. From the numerical model, the effect of gas pressure upon diffusivities were studied and it was concluded that bulk diffusion was the dominant gas flow mechanism. Busch et al. [18] studied the sorption kinetics of methane and CO_2 on Pennsylvanian coals (from the Upper Silesian Basin, Poland) of varying grain sizes ranging from < 0.063 to ~ 3 mm and at temperatures of 318.15 and 305.15 K. It was reported that CO_2 sorption rate was faster by a factor of 2–3 (for moist samples by a factor of 5–6) than that of methane. The bidisperse pore diffusion model was used to analyze the methane and CO_2 sorption kinetic data. It was observed that the bidisperse model did not give adequate fit to the experimental data. The lack of fit of the bidisperse model with the experimental data was attributed to the assumptions of the model, that is, linear isotherms, which are not true for CO_2 and CH_4 adsorption on coal. Cui et al. [19] studied the adsorption kinetics data of methane, CO_2 and nitrogen on coal by analyzing the experimental data using the bidisperse model. It was inferred that the relative adsorbate molecule size and pore structure are the controlling parameters in selective gas adsorption and diffusion in micropores. The micropore diffusivity of CO_2 was higher than methane and nitrogen by one or two order of magnitude because of the smaller kinetic diameter of CO_2 (0.33 nm) than that of N_2 (0.36 nm) and CH_4 (0.38 nm). It was concluded that with increase in pressure the apparent diffusivity decreased, which may be due to coal matrix swelling caused as a result of gas adsorption. The N_2 adsorption kinetic data matched well with the bidisperse model compared to that of methane adsorption rate data and the CO_2 adsorption rate data deviated from the bidisperse model. Saghafi et al. [20] measured the adsorption and diffusion of CO_2 on coal samples from Sydney Basin, Australia. No correlation was observed between the diffusivity and the depth or rank of coals. Mianowski and Marecka [21] studied the applicability of methane and CO_2 kinetics data on the unipore model for heterogeneous coals. It was reported that the experimental data did not match the unipore model for the entire time range. Hence, a modified unipore model was proposed by introducing a diffusion parameter which gave good matching.

Javadpour et al. [22] studied the diffusion of gas in shales from Western Canadian Sedimentary Basin (WCSB) and suggested that a combination of a nanopore network connected to a micrometre pore network controls the gas flow in shale. It was concluded that diffusion coefficient was lying in the range of Knudsen diffusivity (10^{-3}–10^{-1}) suggesting occurrence of slip boundary condition at the nanopore surfaces. Charrière et al. [23] conducted adsorption kinetic experiments of CO_2 and methane on coal from Lorraine basin, France at two pressure steps of 0.1 MPa and 5.0 MPa and at different temperatures (varying in the range of 283.15–333.15 K). It was observed that the sorption equilibrium for CO_2 reached faster than methane and equilibrium time decreased with increasing pressure. It was observed that the effective diffusivity (D_e) and diffusion coefficient (D) determined by assuming Fickian and unipore diffusion increased with temperature. Pillalamarry et al. [24] discussed the diffusion behavior of methane in Illinois basin coals. The (ad/de)sorption data was modeled using Langmuir isotherm model and D was estimated from the experimental sorption kinetic data using unipore diffusion model. It was observed that D decreased with pressure (P) (for pressures below 3.5 MPa) and beyond that (for higher pressures), D did not decrease further and attained a constant value. Hildenbrand et al. [25] reviewed the mechanisms and processes (viscous flow, diffusion, sorption, desorption) affecting transport in unconventional reservoir rocks. It was observed that gas transport in the matrix of coal or shales is strongly controlled by diffusion. Based on the type of gas (methane or CO_2) used, flow may be affected by sorption. Darabi et al. [26] studied the gas flow processes in ultra-tight porous media in which the matrix pore network is composed of nanometre- to micrometre-size pores. A new permeability model was developed and compared it with numerical solution for understanding the gas flow through an inter-connected network of micropores and nanopores, assuming slip flow, Knudsen diffusion, and surface pore roughness. It was observed that the analytical and numerical solutions matched the pressure decay data. Knudsen diffusion was concluded to be the dominant mechanism with 20% contribution in gas flow through shale matrix.

Bhowmik and Dutta [27] conducted adsorption kinetic experiments on coal samples from Jharia and Raniganj coalfields, India. It was observed that rate of adsorption for CO_2 was higher than that of methane and equilibrium for CO_2 reached earlier than methane. With increase in pressure, the rate of adsorption and diffusion decreased. Unipore diffusion model failed to predict the experimental adsorption kinetics data for the entire time range (the model gave fit up to $V_t/V_\infty \approx 0.4$–0.65 for methane, and for CO_2, $V_t/V_\infty \approx 0.3$–0.6). The modified unipore model fitted the adsorption rate data better at various pressure stages for the entire time range. Yuan et al. [10] investigated the methane diffusion behavior in shale from Sichuan Basin, China and also studied the effect of particle size on gas adsorption and diffusion. It was observed that the experimental sorption rate data matched with bidisperse model. It was reported that both the Fickian diffusion (within macropores) and the Knudsen diffusion (within micropores) were dominating the transport of gas in shale. Further, diffusivity was reported to be independent of particle size but was time-dependent.

From the above discussion, it is clear that diffusion is one of the main control parameters for flow of methane/CO_2 in shales and needs to be studied. In the previous studies, unipore model, bidisperse model and MM model were commonly used to describe sorption kinetics data of coal and shales. Unipore model has mostly been used for its mathematical simplicity although it gives good matching mostly in the initial time range. Bidisperse model was mathematically complex and needed pore characterization data. The modified unipore model (MM model)