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Measurement of dynamic adsorption–diffusion process of methane in shale

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HIGHLIGHTS

- Gas dynamic adsorption–diffusion process in shale was investigated.
- Effects of pressure, temperature, particle size and total organic carbon were investigated.
- Adsorption rate constant as a function of pressure and temperature were obtained.

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ABSTRACT

Shale gas is becoming an increasingly important energy resource in recent years. Identifying the gas transport process in a shale matrix is therefore of great importance in designing development strategies and in formulating the appropriate predictive mathematical models. Experimental and numerical investigations were conducted to study gas transport in shale. This paper presents the experimental work and obtains two characteristic parameters from the test results which will be utilized to serve the numerical work. Of great relevance to field development and management is knowing the contribution of each gas source to gas transport history and to ultimate gas recovery. Shale samples from Sichuan Basin in China were studied at designed conditions to test the effect of boundary pressure, temperature, particle size, and total organic content (TOC) on the dynamic adsorption–diffusion process. The tests for crushed shale samples were conducted at 35 °C, 40 °C, and 45 °C, and at test pressures up to 17 MPag. By plotting a curve describing the gas volume change per unit mass at standard condition over time (V_{ad}), the adsorption–diffusion process at isothermal and constant boundary pressure (ICBP) was investigated and interpreted. These results indicate that both higher pressures and higher temperatures could promote a faster adsorption–diffusion rate, thus could promote a greater adsorption constant rate. Higher temperatures caused less gas to be adsorbed into the shale particles. Under the same experimental conditions, a difference in particle size showed no influence on the amount of gas adsorbed, but had a significant effect on the dynamic adsorption–diffusion process: the processing time extended linearly with the diameter of the particle size.

1. Introduction

"Shale gas reservoir" refers to an unconventional hydrocarbon formation that is composed of an ultra-low permeability matrix with nano- to micropores, organic material, and natural and artificial fractures [1,2]. From the 1980s, methane began to be recognized as a fuel that is more environmentally friendly than other fossil fuels [3]. As one of the main sources of methane, shale gas production has become a major source of natural gas in America since the last century, which has a beneficial impact on supplies and consumer prices of natural gas, and increasing exploration of this energy is progressing worldwide. Shale gas exists in large quantities all over the world (in about 137 formations), and amounts to approximately 7299 trillion cubic feet according to the U.S. Energy Information Agency [4], and this amount continues to grow as new reservoirs are discovered.

The gas retained in a shale reservoir is a function of the reservoir pressure, temperature, the mineral content, and the pore

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structure of the reservoir [5]. Due to the complex composition and the multi-scale structure of a shale gas reservoir, the total gas storage capacity arises from three sources: adsorbed gas, free gas, and dissolved gas [6,7]. We will show in this paper that all of these types of gas are involved in the total gas flow rate; hence, production data analysis should include all of these processes. The storage capacities of these three sources vary according to different storage mechanisms. Different from a tight gas reservoir, the adsorbed gas amount plays an important role regarding gas-in-place (GIP) as well as the gas transport process in a shale gas reservoir, with that adsorbed gas amount varying from 15% to 85% of the GIP [8–10]. Therefore, the effect of the adsorbed gas on gas transport is the main issue encountered in shale gas resource evaluation and subsequent development. However, the present research concerning shale reservoirs predominantly focuses on the estimation of reserves. Considering the large amount of adsorbed gas stored in shale matrix, the contribution of the adsorbed gas in shale matrix to the total production is very important.

Gas transport process in shale contains free gas diffusion in the pore channel, gas adsorption on the surface of organic matter or clay mineral content and gas dissolution process in the organic matter [27]. The theory of Langmuir adsorption [3,11,12,27] is often used in adsorption process. The mechanisms of gas diffusion in shale reservoirs have been studied theoretically. Javapour et al. [6], for the first time, systematically introduced Knudsen mechanism into the gas diffusion in shale when the diameter of the flow channel has the same order as the mean free path of the gas molecules. Javapour [19] further proposed a diffusion model for shale gas containing viscous diffusion and Knudsen diffusion. These two diffusion mechanisms were coupled in the form of linear summation. The viscous diffusion in the model was corrected by slip effect. Based on Beskok and Karniadakis's [20] diffusion model and Florence et al.'s [21] extension, Civan [23] coupled the mechanisms of viscous diffusion and Knudsen diffusion through a function of Knudsen number in the form of product. Freeman et al. [13] and Yao et al. [14] mixed the diffusion mechanisms through dusty gas model (DGM) [15]. Except Knudsen diffusion and viscous diffusion, configurational diffusion and surface diffusion may also play an important role in gas diffusion in shale [13,16]. These mechanisms were also applied in dual-porosity model for shale gas reservoir to analyze production process [17,22]. Etminan [7] discussed the theory of gas dissolution process through second Fick's law [18]. Very few of experimental research has been conducted investigating the dynamic gas transport process in shale. Hence, there is a tremendous need to improve our understanding of the gas transport in a shale matrix by experiment so as to better understand the gas transport production and development strategy [24].

The free gas in shale can be calculated by knowing the size of the reservoir, the porosity, and the initial reservoir pressure and temperature. Thus, the total geological resource could be predicted by knowing the amount of adsorbed gas. Many studies have been conducted on assessing the amount of gas adsorbed [25]. The most common technique utilized is the adsorption isotherm, which has been addressed by a valuable body of literature [26–28]. Based on this technique, the adsorbed gas amount at each equilibrium pressure can be obtained. As well, the effects of many factors (such as pressure, temperature, TOC, and kerogen type) on the adsorbed gas volume have been experimentally investigated [29,30]. Pressure is one of the most important factors influencing the occurrence of gas in a shale reservoir. The total adsorbed gas content of shale rises with increasing pressure until it reaches the saturation pressure [31–33]. This is because, at low pressure, gas adsorption requires a high binding energy; as pressure increases, the required binding energy continually decreases and gas adsorption content increases accordingly [34]. Temperature is another important factor, since adsorption is an exothermic process. The adsorbed gas content of shale rises with decreasing temperature [27,29,35]. Different from coal seams, the effect of particle size on the specific surface of shale is negligible, thus it has little effect on the gas adsorption content of shale [36].

Recent experimental and theoretical methods have been adapted from well-established tight gas and coal bed methane (CBM) techniques to study shale gas systems. However, because of the complexities in shale gas reservoirs, the techniques from tight gas and CBM need to be improved and new methodologies need to be developed in order to better understand shale gas systems. The adsorption isotherm provides an indication of how much gas can be adsorbed for a given set of state variables (specifically, at a given pressure and temperature). However, since the adsorption isotherm is just a relationship between the equilibrium adsorption and the pressure, it cannot describe or provide any details of the dynamic (time dependency) gas adsorption–diffusion process, such as the dynamic change between equilibrium adsorptions V_1 and V_2 as schematically shown in Fig. 1. The particles of the shale samples used in this study are assumed to be in spherical shape. The pressure at the particle surfaces (i.e., the pressure set in the sample cell) is defined as boundary pressure. For an adsorption isotherm, the reported pressure is the cell pressure when the adsorption reaches equilibrium. While in the field production, the down-hole pressure of a shale gas well, that is the boundary pressure at the production surface, is expected to be constant for a production period. However, the pressure inside the reservoir keeps decreasing from the original reservoir pressure to the boundary pressure. During this dynamic process, the desorption of the adsorbed gas is not in equilibrium with the pressure and cannot be described by an adsorption isotherm curve. This paper will obtain results showing the dynamic adsorption–diffusion process at isothermal and constant boundary pressure (ICBP) conditions.

When pressure increases, both the free gas in pore space and the adsorbed gas on the pore surfaces will increase. Fig. 2 shows the pressure distribution throughout the matrix at different time of the test at ICBP conditions, which directly governs the gas transport in shale. The x-axis r refers to the distance from the boundary ($r = r_o$) to the particle center (the center of each sphere). The shale sphere is initially saturated with methane in a cell at the initial pressure P_i. To start the adsorption–diffusion test, the cell pressure is suddenly elevated to a higher pressure P_b at $t = t_0$. When the pressure at the surface of the sphere or the boundary pressure P_b is kept constant, the gas starts to transport from the cell to the inside of the sphere. To keep the cell pressure or the boundary

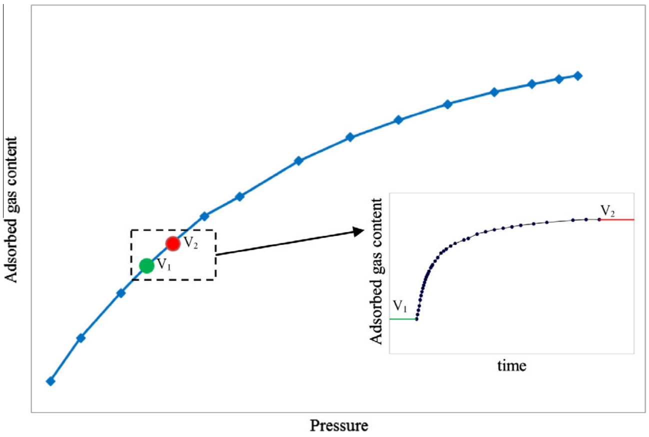

Fig. 1. Interpretation of the dynamic process illustrated by the data points in an adsorption isotherm curve at ICBP.