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Experimental investigation of gas mass transport and diffusion coefficients in porous media with nanopores

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ABSTRACT

Understanding gas mass transport and determining diffusion coefficients are essential for investigating the gas flow mechanisms and evaluating porous media with nanopores. Multiple gas transport mechanisms coexist in porous media with complex pore size distribution, including viscous flow, Knudsen diffusion and surface diffusion. During pressure depletion of a reservoir, the adsorbed gas desorbs into pore space as additional 'free gas', and meanwhile, diffuses along the surface of nanopores in porous media. The surface diffusion itself increases the total gas transport capacity in pores and its effect cannot be neglected. The bulk gas transport (non-surface diffusion) data was excluded experimentally to intensively investigate the surface diffusion during gas mass transport based on the gas storage and flow mechanisms. Accordingly, a mathematical model is developed by incorporating the surface diffusion. The results show that the equilibrium time for gas transport process decreases quickly with temperature. Higher saturation pressure could accelerate the process and increase the amount of produced gas. Besides, the two-stage process of the gas mass transport can be identified by recording the decay of gas pressure, which implies that the surface diffusion dominates the late stage of the gas mass transport. The surface diffusion coefficient for shale is between 10^{-18} and 10^{-16} m^2/s. This study provides a straightforward method to describe the gas mass transport in shale, simple but information–rich for the assessment of shale gas targets.

1. Introduction

Shale, as one kind of porous media which is rich in nanopores, has been playing an increasingly important role in the energy industry and gradually contributes more to the energy supply of the world [1]. Although many ways have been used to improve the recovery of shale gas reservoir such as hydraulic fracturing [2], gas recovery is still less than 6% for shale wells in China [3]. Complex gas flow process happens in shale due to the nanopores introduced in this porous medium. One of the issues yet to be addressed is the mechanisms of the gas mass transport in porous media with nanopores which would be beneficial for enhancing the gas recovery to satisfy the domestic energy demand.

Due to complex pore size distribution and different gas-storage processes, multiple gas transport mechanisms coexist in shale gas reservoirs, including Fick's diffusion and Knudsen diffusion for free gas in inorganic pores, and surface diffusion for adsorbed gas in organic pores [4,5]. Different from conventional reservoirs, the pore size distribution for shale is wide (ranging from nanometers to milimeters) and many nanopores primarily exists in kerogen [6,7]. 15–70% of the total gas in shale reservoir is mainly adsorbed on the surface of nanopores and will influence the production dynamic tremendously [8]. With the development of science and technology, more and more attention has been paid to nanopores and the gas-solid interaction phenomena [9–11]. Consequently, clear gas transport mechanism, mass flow rate and diffusion coefficient will contribute a lot to the development of the shale gas reservoir.

Worldwide research groups have addressed porous media-related (rich in nanopores) problems using different approaches, and the outputs of experimental results are steadily increasing [12–14]. Experimental methods for the measurement of the gas transportation in sub-micron pores includes variable-volume volumetric method (VVM) [12], constant-volume volumetric method

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(CVM) [13], and pulse-decay method (PDM) [14]. The core of the VVM is to describe the dynamic gas storing/producing process when the temperature and the external pressure keep constant. Based on VVM and its mathematical model, the gas transport process can be divided into two stages and the apparent diffusion coefficients can be obtained. While for CVM method, it is mostly used for obtaining the adsorption isotherm curve when the system volume is constant while the pressure changes. Besides, by monitoring the pressure history, the gas transport in sub-micron pore is reflected and the transport stages can be obtained accordingly. PDM is a popular method for measuring the permeability of a core and the production process while the pressure keeps decreasing. Gas flow in porous media with micro/nano pores is considered as a combined result of free gas flow inside the pore and surface transport of the adsorbed gas along the solid wall [15]. Holt et al. [16] reported that in carbon nanotubes less than 2 nm in diameter, the measured CH_4 flow rate exceeds predictions of the Knudsen diffusion model by more than an order of magnitude, which most likely resulted from surface diffusion. However, all the above mentioned methods cannot show any hint of investigating the surface diffusion while gas production.

The driving force for surface diffusion is the concentration gradient. Since the adsorbed gas on organic pore walls has a large concentration gradient during the gas production process [17], the surface diffusion is a very important transport mechanism and cannot be neglected [10,18]. Some researchers stated that, compared with the bulk gas transport, surface diffusion in shale is more significant and even dominates the gas transport [19]. Darabi et al. [20] and Majumder et al. [21] concluded that the presence of surface diffusion can make the apparent diffusivity tens or even several orders of magnitude lower than that predicted by conventional hydrodynamic methods. Many experimental works have been conducted to measure the gas diffusion coefficients in mudstone, coal and shale. In these rocks, the measured diffusion coefficients range from 10^{-12} to 1 m^2/s depending on different types of rock and testing methods [22,23]. Besides, the existed methods usually calculated the apparent coefficient which includes the process of Fick diffusion, Knudsen diffusion, and surface diffusion. However, the effects of surface diffusion and the roles of pressure and temperature on the gas mass transport have not been fully investigated. Specific method is still needed in order to measure the surface diffusion coefficient in shale.

By referring to the organic rich porous media, mathematical simulation works are conducted to explore the gas flow behaviors through the nanopores [3,24–28]. The pore scale of the porous media determines the dominant mechanism of the gas flow process, Fick's diffusion, Knudsen diffusion or surface diffusion, which is distinguished either by collision between molecules, by collision between molecules and pore walls, or by movement along the surface. Gas transport mechanism in conventional reservoir with large pores is dominated by viscous flow which can be described by Darcy's law. However, in the tight gas reservoir gas transport is the combination of Fick's and Knudsen diffusions [24]. In shale gas reservoir, except for the above mentioned mechanisms, surface diffusion along the adsorbed layer should also be considered [11,15,25]. Several mass transport models were accomplished to quantify gas transport considering the adsorbed gas existed in nanopores of porous media [26]. Carlson and Mercer [27] employed Langmuir isotherm theory to consider the effect of desorption behavior of shale gas and described the effect of diffusion by Fick's law. Javadpour et al. [28] described gas flow in nanopores using a diffusive transport regime with a Knudsen diffusion coefficient and negligible viscous effects. Civan [7] coupled the mechanisms of viscous diffusion and Knudsen diffusion through a function of the Knudsen number (Kn) in the form of a product. Wu [3] calculated weighting coefficients of viscous flow and Knudsen diffusion based on probabilities of gas molecules colliding with each other and with nanopore walls. Chen and Yang [29] used the kinetic method to derive the surface diffusion coefficient. They assume all the gas production comes from the adsorbed gas by surface diffusion after a certain period, which might overestimate the surface diffusion coefficient. Fractal models were employed to investigate the gas mass transport in porous media. Yu and Cheng [30] developed a fractal permeability model for bi-dispersed porous media. The model took into consideration of the non-uniform pore sizes and contained no empirical constants. Albaalbaki et al. [31] proposed a model which developed an interfacial boundary condition for diffusion, considering thermodynamic equilibrium, surface diffusion and interfacial exchange kinetics. It can be found that studies on the influence of the adsorbed layer on surface diffusion are rather scanty, and in the few currently published studies, not accurate calculation of surface diffusion coefficient limits those models for practical application with production prediction. The surface diffusion coefficient can be several orders of magnitude smaller than the apparent or effective diffusivity. It is a fundamental scientific problem that how surface diffusion is depicted and how much surface diffusion contributes during gas production, which still needs to be further explored. Therefore, in order to reasonably analyze gas mass transport and accurately forecast gas well deliverability, the surface diffusion must be considered in modelling the mass transport of shale reservoirs.

In this paper, we investigate the gas mass transport behavior in porous shale. Experimental study on the gas mass transport and a model for determining the diffusion coefficient are presented which provide the fundament for numerical simulation and production forecast. First, the proposed experimental method enables the measurement of the dynamic gas mass transport when desorption massively occurs. Tests with helium (He) represent gas flow in porous media in the form of free gas, while tests with methane (CH_4) represent the gas flow process including Fick's diffusion and Knudsen diffusion for free gas, and surface diffusion for adsorbed gas. Second, we examine the effect of temperature and pressure on the gas flow behavior and the diffusion coefficient. Forty flow tests in total are shown under five pressures and four temperatures. Furthermore, a unified model is presented for depicting the gas transport mechanisms including the surface diffusion. By fitting the model with experimental results, the surface diffusion coefficient is obtained. Most importantly, the effect of pressure and temperature on the surface diffusion coefficient is described and analyzed. The experimental determination of the surface diffusion coefficient can depict the clear and accurate effect of parameters and provide more meaningful hint for the production of the shale gas reservoirs.

2. Experiment

2.1. Material

Experiments were conducted to measure the characterization of shale sample and to investigate the gas mass transport through porous media. Since shale is a typical porous media with nanopores with large amount of adsorbed gas in it, shale is chosen as the test sample in this study. The shale samples are collected from Silurian age of Lower Jurassic Formation, Sichuan fold belt in China. The thickness of formation investigated is higher than 100 m, at depths between 585 and 643 m. The permeability of the sample is 3.8×10^{-6} mD with the average porosity 3.76%. According to the XRD test results and Rock Eval measurements, the dominant mineral for tested shale sample is quartz with an average of 48 wt%, followed by clay with an average of 41 wt%. The total organic carbon (TOC) is 1.58 wt%. The particles of the shale sample