Experimental study and modelling of methane adsorption and diffusion in shale

Weina Yuan [a,b], Zhejun Pan [b,*], Xiao Li [a], Yunxia Yang [b], Chunxia Zhao [b,c], Luke D. Connell [b], Shouding Li [a], Jianming He [a]

[a] Key Laboratory of Engineering Geomechanics, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
[b] CSIRO Earth Science and Resource Engineering, Private Bag 10, Clayton South, Victoria 3169, Australia
[c] School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

HIGHLIGHTS

- Experimental study of methane storage and diffusion in shale.
- Pore size distribution was studied using N_2 adsorption and SEM.
- Bidisperse model was applied to describe the diffusion data.
- Sample particle size has little effect on gas storage and diffusion measurement.
- Moisture reduces gas storage and diffusion rate significantly.

ARTICLE INFO

ABSTRACT

Understanding gas storage and transport mechanisms in shale is crucial for reservoir evaluation and gas production forecast. The shale matrix has a complex pore structure, with sizes ranging from nanometres to micrometres. Although diffusion plays a significant role in shale gas transport in the reservoir, systematic studies of gas diffusion in shale are rare. This paper studied the methane diffusion behaviour of shale based on pore structure, as well as the effects of sample particle size and water on gas adsorption and diffusion. The combined N_2 adsorption and SEM experimental results showed that the shale sample had a bimodal pore size distribution. The diffusion data were able to be described adequately by the bidisperse model, and the parameters were consistent with pore size distribution results obtained from the N_2 adsorption and SEM results. It was found that both Fickian diffusion and Knudsen diffusion play important roles in shale gas diffusion and they show different gas pressure dependence. Adsorption isotherm and calculated diffusivity showed little particle size dependence. However, gas adsorption and diffusivity were significantly reduced in moist samples, showing that water reduces gas storage capacity and transport rate in shale.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The rising worldwide demand for natural gas and the difficulty in finding additional large conventional gas fields have stimulated the exploitation of unconventional gas reservoirs. Shale gas is one of the most promising unconventional natural gas resources, with huge reserves located around the world. The production of gas from shale has increased drastically in North America in recent years, due to advanced technologies such as horizontal drilling and multi-staged hydraulic fracturing [1]. Shale gas reserves are also being actively explored in China, Australia, Europe and many other countries [2]. However, shale gas reservoirs are complex and heterogeneous geologic systems, and reservoir conditions are unlikely to be consistent in different areas [3,4]. This makes it difficult to apply existing knowledge to other countries or basins where exploration is still in the early stages. Considerable international efforts are therefore underway to make this resource successfully and economically available. Understanding gas storage and transport in shale sediments is key to future gas production. This knowledge is also needed for analysing reservoir accumulation mechanisms, evaluating shale formations, and optimising production strategies [5,6].

Gas storage and transport differ significantly in shale and conventional gas reservoirs. Shale is both the source rock and the reservoir and can be regarded as fractured with porous matrix. Shale gas occurs as free gas stored in the matrix pores and natural fractures within the shale, and as adsorbed gas on the surface of

* Corresponding author. Tel.: +61 3 9545 8394; fax: +61 9545 8380.
 E-mail address: Zhejun.Pan@csiro.au (Z. Pan).

pores within organic matter and clay minerals in the matrix. It is also possibly dissolved in the shale [7]. To a large extent, the storage and transport of gas in the shale matrix is controlled by pore structure [8,9]. A large proportion of pores within shale matrix are nano-sized, and most of these small pores are associated with organic matter and clay minerals [10–15]. Gas flow in nanopores is likely to be controlled by diffusion, rather than by viscous flow [16]. In contrast, gas flow in natural and hydraulic fractures is Darcian [17]. The shale matrix is often very tightly packed, which makes gas transport within the matrix difficult. Gas diffusion in the matrix could therefore limit gas production rate, making the study of diffusion of great importance for shale gas production. Another influencing factor to gas production is the presence of water in the shale. In shale gas production, a large proportion of fracturing fluid may not flow back and is trapped in shale reservoir [18]. The water in the fracturing fluid that remains in the reservoir may reduce the gas transport rate in the shale.

Some researchers have recently studied shale gas adsorption characteristics and their influencing factors, such as pore structure, organic matter or clay mineral content [7,8,19–24]. The importance of diffusion has also been realised [25–28], and a small number of gas transport models have been applied [29–32]. However, systematic studies of gas diffusion in shale are rare. Many issues, such as gas diffusion models, diffusion mechanisms and water effects, still require further investigation. Given the complexity of the pore system within the shale matrix, diffusion mechanisms could be very complicated [28–31]. Three types of mechanisms could play a role in the gas diffusion in shale: Fickian diffusion, Knudsen diffusion and surface diffusion [33].

In this work, we investigated gas adsorption and diffusion behaviours in shale through experimental studies and modelling. The pore structure of shale was investigated first, because it is a controlling factor of gas adsorption and diffusion. The effects of moisture and particle size on adsorption and diffusion were then investigated by measuring methane adsorption in dry and moist shale samples with three different particle sizes. Then unipore and bidisperse diffusion models were used to describe the diffusion data and to obtain the diffusivity. Lastly, the relationships between diffusivity, pore size, pressure, particle size and moisture content were discussed.

2. Experimental methods

2.1. Shale sample preparation

A shale core obtained from the depth of about 2156 m in the Sichuan Basin of China was prepared for the experimental work. The Sichuan Basin is located within Sichuan Province and Chongqing Municipality in Southwest China. It is tectonically situated in the northwest of the Yangtze metaplatform and surrounded by the Yunnan–Guizhou–Sichuan–Hubei platform fold zone [24]. In Sichuan Basin, shales from six Periods were deposited: Lower Cambrian, Lower Silurian, Lower Permian, Lower Jurassic, Upper Permian and Upper Triassic. Shale of the first four Periods are mainly dark pelitic rock and argillaceous limestone, while the rest two are mainly black pelitic rock and coal rock [4]. The sample studied in this work is Lower Silurian shale and it has been considered to be an effective source rock for shale gas [24,34]. Mineral content of the shale is presented in Table 1.

Part of the sample was prepared for scanning electron microscope (SEM) analysis. The remaining sample was crushed into powder for adsorption measurements. Crushed samples were sieved to three particle sizes: 0.3–0.5 mm, 0.212–0.3 mm and <0.212 mm for CH_4 adsorption and diffusion measurements. Dry samples were prepared under vacuum for 24 h at 105 °C. Moist samples were prepared following the American Society for Testing and Materials (ASTM) procedure. The samples were moistened by placing them in a closed environment next to a saturated solution of K_2SO_4, which provides an atmosphere of about 97% relative humidity at room temperature.

2.2. Pore structure characterisation

Shale matrix has a complex pore structure, with pore sizes ranging from nanometres to micrometres. Many different methods have been used to study the pore structure of shale. These include small angle X-ray and neutron scattering, SEM, SEM combined with focused ion beam, transmission SEM, nuclear magnetic resonance spectroscopy, mercury injection capillary pressure and gas adsorption/desorption analyses [10–13,35–38]. In this work, the morphology of the sample surface was observed using a SEM. Energy dispersive spectroscopy was also combined with SEM to identify the minerals in shale. The surface area and pore size distribution was measured by N_2 adsorption at 77 K using a Micromeritics TriStar 3000 surface area and porosity analyser. The surface area was extracted from the N_2 isotherm at a relative pressure of $p/p_0 = 0.14$. Pore size distribution was calculated by using Barret–Joyner–Halenda (BJH) method.

2.3. Diffusion and isotherm measurement

CH_4 adsorption and diffusion experiments were conducted on a Hy-Energy PCTPro–E&E apparatus, which uses a manometric method. Due to the low gas adsorption in shale, a micro-doser was therefore used in the experiments to increase accuracy. Adsorption isotherms were measured to a maximum gas pressure of about 33 bar with a pressure step of about 5 bar. For adsorption kinetic measurement, pressure change against time was recorded at each pressure step; every 0.3 s at the beginning, and then at increased intervals for a period of 2 h to ensure full equilibrium was reached. All experiments were conducted at 26 °C.

The amount of adsorption calculated from the experimental data is the excess adsorption. Eq. (1) was used to convert excess adsorption to absolute adsorption [39]:

$$n_{ads}^{Abs} = \frac{n_{ads}^{Excess}}{1 - \rho_{gas}/\rho_{ads}} \tag{1}$$

where n_{ads}^{Abs} is the absolute adsorption amount, n_{ads}^{Excess} is the excess adsorption amount, ρ_{ads} is the adsorbed phase density (0.421 g/ml is used for CH_4 in this work), and ρ_{gas} is the gas phase density, which was calculated from the National Institute of Standards and Technology WebBook (http://webbook.nist.gov/chemistry/fluid).

The pores of shale also contain free gas. The amount of free gas at each pressure step was calculated by:

$$n_{free} = \rho_{gas}(V_{pore} - n_{ads}^{Abs}/\rho_{ads}) \tag{2}$$

where n_{free} is the mass of the free gas and V_{pore} is pore volume per unit sample prior to gas adsorption.

Table 1
Mineral content of the shale sample.

Sample	Quartz (%)	Clay minerals (%)	Organic matter (%)	Albite (%)	Pyrite (%)	Calcite (%)	Potash feldspar (%)	Others (%)
Lower silurian shale	48.9	28.5	6.3	9.8	3.1	2.0	1.0	0.4