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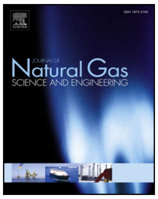

Gas slippage in fractal porous material

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ABSTRACT

Gas flow through porous media in the slip flow regime is of great significance for the exploitation of underground natural gas and oil. The gas slip effect in porous media plays a very important role in different engineering fields, because gas slippage is involved in the determination of gas apparent permeability. In this study, the gas slip effect was investigated in model microporous materials: composite silica aerogels. We measured gas and water permeability in sets of nano composite silica aerogels, fractal materials with a high pore volume and tortuosity, and low permeability. The observed difference in gas and water permeability was analyzed from the point of view of the slip regime (Klinkenberg correction), *b*) and transition regime (Knudsen correction). The effect of structural parameters of porous media (pore volume, tortuosity, fractal features) on the Klinkenberg and Knudsen corrections are discussed and the different models proposed in the literature are tested. Experimental results showed that: (1) gas permeability is almost two orders of magnitude greater than water permeability, (2) Klinkenberg and Knudsen corrections increase with decreasing permeability, (3) the Knudsen corrections calculated from the literature models were almost one order of magnitude lower than experimental data, (4) we also tested the Klinkenberg approach for tortuous and fractal porous media, the fractal model with second-order slip improved the accuracy of the prediction and agree with the experimental results.

1. Introduction

Producing gas from shale strata has been playing an increasingly important role in the energy sector (Wang and Krupnick, 2013). There has been a rapid increase in production from unconventional condensate and gas resources. Due to the importance of these low permeability reservoirs in gas production, extensive research and models has been conducted on these types of resource (Javadpour, 2009 2; Swami, 2012; Scheidegger, 1974; Li et al., 2017a, 2017b). The physics of flow through porous media has received considerable attention due to applications in soil mechanics, groundwater hydrology, petroleum engineering, water purification and different empirical approaches have been used to describe the observed nonlinear dependence of permeability with porosity (Javadpour et al., 2007; Johnson et al., 1990; Panday et al.,1995; Loosveldt et al., 2002; Lysenko et al., 2004; Bear, 1972; woods et al., 2011; Florence et al., 2007; Pape et al., 1999). For highly permeable porous media, Darcy's law can be applied to describe the relationship between gas flow and pressure gradient, but for low permeable porous media with nanopore size, the measured gas permeability is larger than the intrinsic permeability (Florence et al., 2007). Because of slim throat and low permeability, the gas slip effect controls gas flow behavior and seriously affects the ability of gas to flow in a tight sandstone gas reservoir (Guo et al., 2013, 2015; Li et al., 2016; You et al., 2013). The slip phenomenon means that the velocity of the gas molecules near the pore wall is not equal to zero, and this results in the gas apparent permeability being larger than the intrinsic permeability (Klinkenberg, 1941; Xu, 2014). Loucks et al. (Loucks et al., 2009)) found that gas shale strata are composed of micro and nanopores, the majority being nanopores. The diameters of most pores are concentrated in the range of 1–200 nm (Curtis et al., 2010; Cipolla et al., 2009) and Javadpour (Javadpour et al., 2007) found that the absolute permeability of shale bedrock is less than 150 nanodarcy.

In nanopores, when the mean free path of molecules is in the same order of magnitude as the pore radius, non-Darcy flow occurs. This phenomenon causes an increase in the gas permeability of the flowing fluid. These facts underline the importance of understanding how gas flows in nanopores, which is critical for shale gas simulation and cost-effective commercial production (Sanaei et al., 2014).

Some studies on rocks (Florence et al., 2007; Tanikawa and Shimamoto, 2006, 2009; Heid et al., 1950; Jones, 1972, Jones &

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Owens, 1980; Mc Phee and Arthur, 1991) reported notable discrepancies between permeability measured with gas and that measured with water. As explained above, these discrepancies are related to the dependence of gas permeability on pore size and was analyzed from the point of view of the slip regime (Klinkenberg correction, b) and transition regime (Knudsen correction, fc) (Florence et al., 2007; Civan, 2010; Beskok and Karniadakis, 1999; Ziarani and Aguilera (2012); Anez et al., 2014).

Many natural and artificial porous media have been shown to follow fractal scaling rules (Cai et al.,2014; Thompson et al., 1987; Civan et al., 2011; Geng et al., 2017; Gimenez et al., 1997; Kruhl, 2013; Zheng et al., 2013; Song et al.,2018; Munoz et al., 2014). Porous media found in nature such as soils and sandstones in oil reservoirs consist of numerous irregular pores of different sizes spanning several orders of magnitude in length, and such media were shown to display fractal characteristics (Munoz et al., 2014; Wang et al., 2014; Fu et al., 2005; Thompson et al., 1987; Young and Crawford, 1991; Katz and Thompson, 1985; Yu et al., 2009).

In porous media with multi-scale pore size, fluid flux is known to be affected by transport mechanisms, fluid properties and pore structure properties. Recently the literature (Hu et al., 2013; Zhang et al., 2014) studied the tortuous and fractal characteristics of the pore structure of shale. Beskok and Karniadakis (Beskok and Karniadakis, 1999) developed a unified Hagen–Poiseuille-type model and this model has been adopted by Civan (Civan, 2010; 2011) to precise the effect of porosity, and tortuosity of porous media. Geng et al. (40) developed a fractal model for real gas transport and recently analytical models for gas slippage in fractal porous media were proposed (Zheng et al.,2013; Song et al., 2018).

The gas flow within fractal porous media are modeled by tortuous capillaries with different diameters.

Zheng et al., derived a fractal model for gas slippage factor based on the simplified Beskok et al. model and in a recent study Song et al. (Song et al., 2018) established a fractal model with second-order slip.

These models could be useful to characterize the influence of the tortuosity and the fractalness on the flow in shale or in other fractal porous media. However, they need to be checked on real fractal materials.

Silica aerogel materials, are a class of mesoporous materials with a high specific surface area, a high porosity and data show the silica aerogels have very poor liquid permeability ($\sim 10\,\text{nm}^2$) (Woignier et al.,1990; Scherer, 1989, 1991; 1992; Beurroies et al., 1995; Kong et al., 1993; Reichenauer et al., 1995). Last but not least, these materials have a fractal structure with a fractal dimension ranging from 1.6 to 2.4 depending on the synthesis conditions (Woignier et al., 1990; Marlière et al., 2001).

Therefore, because of their fractal structure and low permeability, aerogels are thus interesting porous structures to test models in the literature that extrapolate gas and liquid permeability from structural parameters. The objectives of this study were thus:

1) To control the gas (K_{gas}) and liquid permeability (K_{liq}) of composite aerogels by the control of the gelation process (adding silica pyrogenic particles to the gel solution);
2) To calculate the Klinkenberg and Knudsen correction factors for the set of aerogels by comparing K_{gas} and K_{liq} data;
3) To compare the calculated corrections factors with model predictions and discuss the corrections factors in terms of porosity, tortuosity and fractal features of the porous structures.

2. Materials and methods

2.1. Synthesis

Nanocomposite silica aerogels were synthesized using the same protocol as for previously published composite gels (Anez et al., 2014; Marlière et al., 2001; Reynes et al., 2001; Toki et al., 1988). First, a wet composite gel was obtained by hydrolysis and polycondensation reactions of organosilicate compounds (tetraethylothosilicate, TEOS) dissolved in ethanol. Pyrogenic silica (aerosil) was added under stirring and the pH was adjusted to 4.5, leading to gelation in a few minutes. The weight of the pyrogenic silica as a percentage of the total silica weight, ranged between 0% and 55%. The nanocomposite-wet gels were then transformed into aerogels by supercritical drying with ethanol (305 °C, 13 MPa).

2.2. Textural characterization

Bulk density (ρ_a) was determined from direct measurements of weight and from the geometric dimensions of samples. Pore volume (V_p) and porosity (ϕ) were calculated from bulk density and skeletal density (ρ_s). The skeletal density, measured by helium pycnometry, was $\rho_s = 2\,\text{g/cm}^3$.

The specific surface area (S) was measured using nitrogen adsorption-desorption (BET analysis) (55) using a MICROMETRICS ASAP 2000. The hydraulic diameter (D_H) was derived from the textural features V_p and S through the relationship (1):

$$D_H = \frac{4V_p}{S} \tag{1}$$

The scanning electron micrographs were obtained with a Cambridge stereo scan 360 scanning electron microscope.

The fractal features of the composite aerogels were characterized by Ultra Small Angle X-Ray Scattering experiments (USAXS). The details of the technique are given in references (Marlière et al., 200163). USAXS experiments give information on three main features of the aerogel structure: the mean size of the aggregates (ξ_{max}) which are connected to form the network, the mean size of the primary particles (ξ_{min}) which stick together to build the aggregates and the fractal dimension D_f which expresses the aggregates compactness (Woignier et al., 1990; Marlière et al., 2001). These experiments characterize the microstructure in the range of the aerogels mesoporosity. In previous study (Marlière et al., 2001), we observed a fractal structure between 10^{-2} and $10^{-4}\,\text{Å}^{-1}$ (length scales in the range of 10–1000 nm). This fractal microstructure have been attributed to the clusters issued from the aggregation of the aerosil particles. The fractal dimension of the aggregates is close to 1.6–1.7, and the fractal range (ξ_{max}/ξ_{min}) is broad, around two orders of magnitude.

2.3. Permeability characterization

The experimental technique used to measure gas permeability K_{gas} is described in (Anez et al., 2014). When compressible gas is used as pore fluid, the one-dimensional homogenous flow through porous media can be written as:

$$K_{gas} = \frac{dV}{dt}\frac{L\mu}{A}\frac{(2P_b)}{(P_1^2 - P_2^2)} \tag{2}$$

where dV/dt is the flow rate or variation in volume (dV) per time unit (dt), μ is the fluid viscosity, A is the sample cross-sectional area to flow, L is the sample length, P_1 is sample intake and P_2 is exhaust pressure, and P_b is atmospheric pressure. Measurements were made with N_2 and the experimental setup (Fig. 1) enabled measurement of K_{gas} over a range of mean pressures of 500–1000 hPa. The experimental data are given for a mean pressure of 900 hPa.

Liquid permeability K_{liq} was measured using a method of impregnation based on Archimedes' principle (Reynes et al., 2001) (Fig. 2). The samples are dipped in water, and when the impregnation proceeds, Archimedes force decreases proportionally to the filled pore volume. During impregnation, the thickness of the penetrating water, h(t), increases with time. We previously showed that: