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Modeling adsorption–desorption hysteresis in shales: Acyclic pore model

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ABSTRACT

Existing conventional measurements face challenges in characterizing transport properties of a shale because they are designed originally for formations with relatively wide pores and high permeability. The integrated analysis of such measurements helps us better understand the connected pore system of a shale formation when they are sensitive to the pore topology and cover a wider range of pore size. Here, we analyze nitrogen adsorption–desorption and mercury intrusion measurements to characterize the pore space of a shale. We determine pore-body size distribution by interpreting adsorption–desorption experiments. We also calculate pore-throat size distribution from mercury intrusion. We adopt the acyclic pore model, which embraces limited pore connectivity, and account for the connected path of the pores at the core scale. Our study distinguishes the pore size relevant to the storage and the flow conductance for the shale.

1. Introduction

Any piece of rock comprises void space and solid grains (non-void regions). In pore-scale modeling [1–6], we analyze the transport properties of the void space at scales smaller than the size of the core (~1 cm) and then relate our analysis to the measurements conducted on the cores. We classify the void space into pore bodies and pore throats and then analyze the interactions between the pores. The pore throat is the narrowest region of the pore space connecting the neighboring pores, whereas the pore body is the wider region of the pore.

Topology of pore space plays an important role in controlling the transport properties [7,8]. Recent advances in acquiring high-resolution images shed light on the pertinent complexity [9,10] but we cannot yet determine the representative size for such images *a priori* [11]. However, the representative size can let us derive a network of the connected pores that can be used for analyzing transport properties at the core scale.

There are few theoretical pore models that account for the effective pore connectivity at the core scale, such as bundle of tubes [12], regular lattice [13], sphere packing [1], multi-type model [14], and acyclic pore model [15–17]. They are physically representative of the pore space because they can capture the transport properties at the core scale. They may not be necessarily representative of the pore connectivity at sub-core scales because we do not test them at those scales. Instead, we usually use core-scale measurements, such as relative permeability [3] and drainage [7,8].

The pore throat is the narrowest region of the pore space connecting adjacent pores and has a dominant effect on the fluid displacement. To determine the pore-throat size distribution for the connected path of the pores at the core scale, we often analyze the drainage data, in which the non-wetting phase displaces the wetting phase. The invasion percolation suggests that the invading fluid displaces the resident fluid when the applied capillary pressure is larger than the critical pressure for the connecting throat. The critical capillary pressure is a functions of the throat curvature that can allow us to determine the pore-throat size distribution using Young–Laplace relation.

The pore volume depends more on the pore-body size. Hence, we can evaluate pore-body size distribution by analyzing adsorbed volume for adsorption–desorption tests. The adsorption begins when the porous medium is exposed to a gas and the molecules adhere to the pore wall. The amount of gas adsorbed is a function of the nature of the solid phase, the gas molecules, the surface area of the solid phase, and the relative pressure.

In an adsorption–desorption test, the variation of adsorbed volume with relative pressure shows hysteresis which is dependent on capillary condensation [18]. In a single conduit, the condensation pressure is a function of the pore-body size, the shape, and the interaction between the fluid and pore wall [19]. In a porous

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medium, the hysteresis is also controlled by pore connectivity [20]. We will take advantage of this dependency for pore space characterization in this study.

Increasing interest in shale formations [21–27] brings up the challenge of estimating former's transport properties, which can be significantly different from those of previously produced formations. As an example, the matrix permeability is usually smaller than 1 μd. The lower permeability can be due to narrower pores and inferior pore connectivity. With this in mind, many people analyzed their pore structures [28–33]. While the conducted studies shed light on the complexity of the pore space, the difference between the pore-body and the pore-throat sizes has not been investigated.

In this paper, we use nitrogen adsorption–desorption isotherms and mercury intrusion capillary pressure measurements to characterize the pore space of a shale. We use acyclic pore model and account for the effective pore connectivity at the core scale [15].

2. Methodology

2.1. Characteristic behavior of a single conduit in adsorption–desorption

We use the Halsey's model to determine the thickness of an adsorbed layer on the pore wall. The Halsey's model relates the thickness of the adsorbed layer to the relative pressure as follows [34]:

$$t = 3.54\left(\frac{-5}{\ln\left(\frac{P}{P_o}\right)}\right)^{1/3} \quad (1)$$

where t is the thickness of the adsorbed layer in Angstroms, P is the gas pressure, and P_o is the saturation pressure.

We can determine the thickness of the adsorbed layer using Halsey's model at small relative pressures (P/P_o). At high relative pressures, Halsey's model is not accurate because it does not account for the condensation and evaporation inside the pore that occur during adsorption and desorption, respectively. The injected gas changes to liquid and fills the capillarity at relative pressures that are higher than the threshold pressure. We determine the threshold relative pressures corresponding to condensation and evaporation as follows [18]:

$$RT\ln\left(\frac{P}{P_o}\right)_{adsorption} = \frac{-\gamma V_{mol}\cos(\theta)}{r_p - t} \quad (2)$$

$$RT\ln\left(\frac{P}{P_o}\right)_{desorption} = \frac{-2\gamma V_{mol}\cos(\theta)}{r_p - t} \quad (3)$$

where R is the gas constant, T is the temperature, γ is the surface tension, $(P/P_o)_{adsorption}$ is the threshold relative pressure corresponding to condensation, $(P/P_o)_{desorption}$ is the threshold relative pressure corresponding to evaporation, V_{mol} is the molar volume of the liquid phase, θ is the contact angle, and r_p is the pore radius. Table 1 lists the pertinent parameters. These relations are relevant to a single conduit, and not to the porous medium.

The thickness of the adsorbed layer on the pore wall is a function of relative pressure (Eq. (1)). The threshold relative pressures relevant to condensation and evaporation are also dependent on the original pore size (Eqs. (2) and (3)). Thus, the original pore size dictates the threshold pressures.

To calculate condensation and evaporation pressures (Eqs. (2) and (3)), we first suppose that the adsorbed layer thickness is negligible ($t = 0$). We then calculate the thickness for the estimated pressures (Eq. (1)). Subsequently, we calculate the pressures using the updated thickness and repeat this process to reach convergence. Fig. 1 presents the results.

The threshold relative pressure can be determined from Fig. 1. In adsorption, there is a sharp increase in relative adsorbed volume at the threshold relative pressure. For instance, the threshold relative pressure is almost equal to 0.55 and 0.87 when the pore size is equal to 3 nm and 20 nm, respectively. There is also a sharp decrease in the adsorbed volume at the threshold relative pressure during desorption. We suppose that the conduit is filled with liquid when the relative pressure is higher than the threshold relative pressure.

We analyze the normalized adsorbed volume (V_n) for a conduit whose pore-body size is smaller than or equal to 130 nm, which is typical for shales. The normalized adsorbed volume is larger for smaller conduits at a given relative pressure (P/P_o). The relative pressure determines the thickness of the adsorbed volume that has a larger volume fraction for narrower conduits. The difference between condensation and evaporation pressures decreases with the conduit size, which shrinks the hysteresis. (Compare the results for 3-nm and 130-nm conduits.) Thus, the difference between adsorption and desorption curves of single a conduit is more significant for narrower conduits.

2.2. Adsorption–desorption measurements

We analyze adsorption–desorption isotherms of shales available in the literature [30,31]. Table 2 lists the pertinent data. We plot the nitrogen isotherms for the shale samples (Fig. 2a and b).

We normalize the measured adsorbed volumes ($V_{exp\text{-}n}$) to analyze the characteristic behavior with relative pressure (Fig. 2c). The hysteresis loop in Fig. 2c suggests the presence of mesopore based on our analysis of a single conduit where condensation and evaporation pressures differ significantly from the bulk saturation pressure. The closure relative pressure is almost equal to 0.45 for all samples and there is no significant difference between the adsorbed volumes determined from adsorption and desorption at relative pressures smaller than this value.

2.3. Acyclic pore model

We use the acyclic pore model [15] to characterize the pore space. There is a unique path between any two points in the model (Fig. 3a) when they are connected [35]. The main feature of the acyclic pore model is that the accessibility of wider pores is not restricted by narrower pores. Narrower pores are accessible from wider throats. Sakhaee-Pour and Bryant [15] showed that the acyclic pore model can capture the drainage experiment when the variation of the capillary pressure with wetting phase saturation exhibits a non-plateau-like trend (Fig. 3b). This allows us to determine the pore-throat size distribution.

Table 1
Input parameters for calculating threshold relative pressures for nitrogen based on Kelvin's model (Eqs. (2) and (3)), and for capillary pressures in mercury intrusion [18].

Nitrogen				Mercury	
R	V_{mol}	γ	θ^o	γ	θ^o
$8.314\ \left(\frac{J}{kmol}\right)$	$3.467\times10^{-5}\ \left(\frac{m^3}{mol}\right)$	$8.85\times10^{-3}\ \left(\frac{N}{m}\right)$	0	$487\times10^{-3}\left(\frac{N}{m}\right)$	140