Relative permeability to water or gas in the presence of hydrates in porous media from critical path analysis

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A B S T R A C T

Most existing models for predicting relative permeability in the presence of hydrate are either empirical or based on simplistic representations of the pore system and hydrate growth. Multiple models are often needed to explain relative permeability behavior observed in the laboratory over different ranges of hydrate saturation. Critical path analysis (CPA) offers a framework for predicting relative permeability based on pore system properties, including the percolation threshold and breadth of the pore size distribution. Using an existing method developed for partially saturated soils, I show that CPA can accurately predict relative permeability to either water or gas over the entire range of measured hydrate saturation for several suites of laboratory measurements. The method does not require any assumption of hydrate growth habit, and assumes that hydrate tends to grow in the largest pores first. This work represents an improvement in understanding the link between pore structure and transport properties of hydrate-bearing sediment.

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1. Introduction

Methane hydrates are solid, crystalline compounds composed of water and methane that are stable at the high pressures and low temperatures typical of the upper ~ 1 km of sediment in deep-water continental margins and sub-permafrost sediment (Kvenvolden, 1998). Hydrates have been the focus of scientific research for many years (e.g., Vasil'ev et al., 1970; Makogon et al., 1972) due to their potential importance to global climate change, carbon cycling, submarine geohazards, and more recently as an energy resource (Kvenvolden, 1988; Dickens et al., 1997; Dickens, 2003; Hornbach et al., 2004; Paull et al., 2007; Boswell and Collett, 2011). The permeability of hydrate-bearing sediments is an important parameter for understanding fluxes of water, dissolved methane, salt, and methane gas, which in turn control rates of pore pressure buildup and dissipation, growth of solid hydrates, carbon cycling, and methane gas production. In particular, the permeability reduction due to growth of hydrate in the pore space exerts a significant control on the timescales associated with these processes (e.g., Nimblett and Ruppel, 2003). This effect is quantified by a relative permeability, which is the ratio of permeability in the presence of hydrates to the intrinsic, hydrate-free permeability of the sediment. Determining the permeability of hydrate-bearing sediments in the laboratory is difficult because it either requires having preserved pressure cores, which can only be analyzed with

very specialized equipment (e.g., Konno et al., 2015; Priest et al., 2015; Santamarina et al., 2015), or forming hydrate in analog materials in the laboratory and measuring permeability, which is time consuming and requires very precise control on pressures and temperatures (e.g., Johnson et al., 2011; Delli and Grozic, 2014). Understanding the permeability of sediments in the presence of hydrates therefore remains an area of active research.

If hydrate saturation (the volume fraction of pore space occupied by hydrate) is known, the change in permeability due to the presence of hydrate may be calculated. Many models exist for computing the relative permeability as a function of hydrate saturation (Fig. 1). The simplest of these models consider the pore system as an idealized network of cylindrical tubes or the interstitial spaces between spherical grains, and invoke different functions for relative permeability depending on whether the hydrate forms preferentially in a grain-coating or pore-filling habit. However, comparison with laboratory measurements performed on the same sample often show that different relative permeability models work better over different ranges of hydrate saturation (e.g., Ordonez et al., 2009; Kumar et al., 2010). To overcome this challenge, Delli and Grozic (2013) proposed a model that is based on a weighted average of relative permeabilities for grain-coating and pore-filling growth habits where the weighting is a function of hydrate saturation. However, their model contains several empirical constants that require tuning to laboratory data and are not strictly related to characteristics of the pore system. Dai and Seol (2014) proposed a model based on simulations in a pore network model with a log-normal distribution of pore sizes

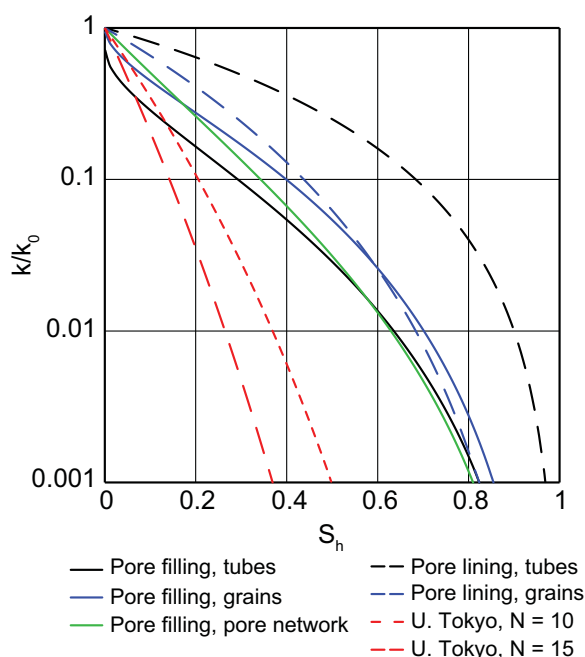E-mail address: daigle@austin.utexas.edu

Fig. 1. Existing models for relative permeability in hydrate-bearing sediments. Hydrate saturation (S_h) is plotted against k/k_0, which is the ratio of the reduced permeability in the presence of hydrate relative to the intrinsic, hydrate-free permeability. Pore filling, tubes: hydrate occupies centers of cylindrical tubes (Kleinberg et al., 2003). Pore filling, grains: hydrate occupies the centers of pores in a pack of spherical grains (Spangenberg, 2001). Pore filling, pore network: hydrate occupies the centers of pores in a network with a distribution of pore sizes (Dai and Seol, 2014). Pore lining, tubes: hydrate coats the walls of cylindrical tubes (Kleinberg et al., 2003). Pore lining, grains: hydrate coats the surfaces of spherical grains (Daigle and Dugan, 2011). University of Tokyo (U. Tokyo) models (Masuda et al., 1997): $k/k_0 = (1-S_h)^N$. $N = 10$ or 15 are recommended to account for preferential accumulation of hydrate in pore throats.

and heterogeneous hydrate distribution that more accurately considers the case of pore-filling hydrate as an analog to capillary drainage. Their model incorporates changes in both pore volume available to flow and tortuosity of flow paths as hydrate saturation increases. However, their model lacks the flexibility required to be able to match laboratory measurements on individual samples or consider different hydrate growth habits. Finally, a common issue with all these relative permeability models is that the relative permeability does not decrease to 0 until hydrate saturation of 100%. This is at odds with the concept of a percolation threshold or irreducible saturation (Amyx et al., 1960; Sahimi, 1993), which should provide a lower limit on water or gas saturation since advective and diffusive supply of methane will not be possible at water saturations below this value (e.g., Sahimi, 1993; Ghanbarian et al., 2015). A unified, physically realistic model for relative permeability in hydrate-bearing sediments would therefore offer a great advantage in predictive capabilities.

Percolation theory and critical path analysis (CPA) allow determination of transport properties of disordered media like soils and rocks based on structural parameters of the pore system such as connectivity and breadth of the pore size distribution (Berkowitz and Balberg, 1993; Friedman and Seaton, 1998; Hunt, 2001). According to percolation theory (Broadbent and Hammersley, 1957), flow of a given phase occurs only when the saturation of that phase exceeds some threshold (the percolation threshold, p_c) that depends on the degree of connectivity of the pore system; better-connected pore systems have lower p_c (Sahimi, 1993). CPA, which was originally developed to describe electrical conductivity in amorphous germanium, silicon, and carbon used in semiconductors (Ambegaokar et al., 1971; Pollak, 1972), states that flow occurs mainly through the highest-conductivity (i.e., largest) pores

such that the fraction of pores contributing to flow is equal to p_c. Hunt, (2005a) and Ghanbarian-Alavijeh and Hunt, (2012) showed that CPA and percolation theory accurately predicted the relative permeability of both air and water in partially saturated soils, and derived equations relating relative permeabilities to p_c and the breadth of the pore size distribution. Here, I show that their results may be applied to laboratory measurements of permeability in hydrate-bearing sediments with a high degree of accuracy. By considering how hydrate grows first in the largest pores, regardless of growth habit, relative permeability may be modeled with a single function of hydrate saturation. This suggests that percolation theory and CPA represent a promising, unified framework for understanding permeability in hydrate-bearing sediments.

2. Background

In this section, I explain how hydrate growth in porous media is similar to a capillary drainage process regardless of growth habit, and I present a relative permeability model based on critical path analysis that has been developed for soils. It is important to note here that this model is only valid for hydrate that is disseminated through the pore space. It is not intended for hydrate that is present as discrete nodules, lenses, or veins. These morphologies are encountered in natural hydrate systems (Waite et al., 2009; Dai et al., 2012) but I do not consider their effect on permeability here.

2.1. Hydrate growth in porous media

The growth habit of hydrate – that is, whether it is pore-filling, grain-coating, grain-cementing, or present in discrete nodules, lenses, or veins – is known to control many physical properties of hydrate-bearing sediment (Waite et al., 2009; Dai et al., 2012). In laboratory studies, the method of hydrate formation has been shown to influence the growth habit. Forming hydrate directly from water with dissolved gas tends to form pore-filling hydrate (Tohidi et al., 2001; Spangenberg et al., 2005; Kerkar et al., 2009), presumably because the centers of larger pores are the most thermodynamically favorable location for hydrate nucleation (Clennell et al., 1999). On the other hand, forming hydrate from water and a free gas phase can result in grain-coating or grain-cementing hydrate since hydrate growth in this case tends to progress from the gas-water interface into the water phase (Zhong and Rogers, 2000; Moon et al., 2003; Jung and Santamarina, 2012; Jin et al., 2012). In natural hydrate accumulations, hydrate growth habit is affected not only by the phase of the supplied methane (dissolved or gaseous) but also by saturation and stress history (Waite et al., 2009). This can result in many complications relative to laboratory investigations. For example, hydrate in sub-permafrost settings may have formed by conversion of existing free gas accumulations (Collett and Ginsburg, 1998; Collett et al., 1999; Boswell et al., 2011), but acoustic data generally indicates that these hydrates tend to exhibit a pore-filling growth habit (Kleinberg et al., 2005; Lee and Collett, 2005). A priori knowledge of growth habit is therefore not generally available, which can make selecting the proper relative permeability function quite difficult.

We can, however, circumvent this problem by considering how the pore size distribution affects hydrate growth. Nucleation of hydrates from water and dissolved methane will tend to fill the largest pores first, leaving only the smaller pores available for fluid flow (Fig. 2a). The localization of hydrate in the larger pores is reinforced by Ostwald ripening, in which larger crystals tend to grow at the expense of smaller ones due to diffusive transport of methane toward the larger crystals (Henry et al., 1999). This will result in relative permeability behavior that is analogous to that of the wetting phase during a conventional capillary drainage