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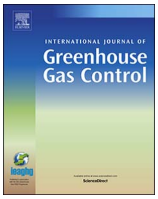

The effect of organic matter and thermal maturity on the wettability of supercritical CO_2 on organic shales

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ABSTRACT

The geologic sequestration of CO_2 is a potential solution for decreasing anthropogenic atmospheric CO_2 emissions by trapping it underground. A primary mechanism for storage is structural trapping where low permeability and high capillary entry pressure caprock materials hold back the buoyant CO_2 from rising to the surface. The wettability (or contact angle) of reservoir and caprock materials in relation to CO_2 and formation brine partly determines the efficiency of structural trapping. Current practice applies the results of individual reservoir-comprising minerals recorded under laboratory conditions, to rocks under in-situ reservoir conditions. However, the wide variety of measured contact angles reported in the literature calls this practice into question. Moreover, organic shales have not been the focus of systematic studies. Here we analyzed the wettability of CO_2 on organic shales at various organic matter concentrations and thermal maturities. We found that bulk organic shale remains highly water wet with respect to CO_2 despite changes to the maturity or concentration of organics. This finding is in contrast to recent molecular dynamic simulations and our initial expectations from previous pore-scale analyses in which organic matter was shown to be hydrophobic. The results are likely due to the remaining mineralogy of the rock dominating the wetting behavior despite concentrations of organics up to 7.9%. This means that reservoirs and aquifers capped by organic rich caprocks may be suitable locations for CO_2 storage and that organic matter at concentrations below percolation threshold may not have a detrimental effect on structural trapping efficiency.

1. Introduction

1.1. Wettability and structural trapping

The sequestration of anthropogenic carbon dioxide (CO_2) in deep geologic formations has been proposed as a method to mitigate further increases in the concentration of atmospheric CO_2. One of many demonstration projects around the world is the “Sleipner project” in the North Sea where one million tons of CO_2 have been injected each year. Recent work on the Sleipner project has revealed the buoyant migration of CO_2 through multiple shale beds due to “unexpectedly low threshold [capillary] pressures for vertical migration” (Cavanagh and Haszeldine, 2014). While the authors conclude these lower threshold pressures are due to micro fractures the wettability of the shale beds should not be disregarded.

The capillary entry pressure (P_c) for buoyant CO_2 to rise through a caprock is controlled by the wettability of the brine, supercritical CO_2 (s-CO_2), and reservoir rock system (brine/s-CO_2/rock). The relationship between the contact angle (θ) and the capillary entry pressure is described by the Young-Laplace Equation (Laplace et al., 1829; Young, 1805)

$$P_c = \frac{2\sigma\cos(\theta)}{r} \tag{1}$$

where σ is the interfacial tension between the two fluids and r is the radius of the capillary. The primary sealing mechanism of a caprock, commonly called “structural trapping”, is therefore related to the wettability of the brine/s-CO_2/caprock system and the radius of the largest connected pore throat. The pressure generated due to the buoyancy of a continuous CO_2 column trapped beneath a caprock is:

$$P_b = (\rho_b - \rho_g)gh \tag{2}$$

where ρ_b is the brine density, ρ_g is the CO_2 density, g is the gravitational acceleration, and h is the height or thickness of the CO_2 plume. By

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equating P_b and P_c we can find the height of a CO_2 plume which can be stored beneath a caprock before CO_2 invasion will occur, so that:

$$h = \frac{2\sigma\cos(\theta)}{(\rho_b - \rho_g)gr} \tag{3}$$

The average radius of a shale pore can vary from 5 nanometers to 100s of nanometers (Nelson, 2009). Assuming shale is water-wet ($\theta < 90°$), these small pores retain buoyant CO_2 directly proportional to P_c; however, if shale is CO_2-wet ($\theta > 90°$), then P_c is negative and the rock may spontaneously imbibe CO_2. A negative P_c is equivalent to a suction force, which would pull CO_2 into the shale caprock.

The breakthrough pressure of a given shale can be calculated using (Eqn 1) with the minimum pore throat radius, r^*, along an interconnected and continuous path of pores across the shale unit. This r^* is usually larger than the mean r and can be related to the mean pore size and the standard deviation of the pore size distribution (Espinoza and Santamarina, 2010). Hildenbrand et al. (2004), conducted CO_2 breakthrough tests on a series of mudstones, sandstones and other sedimentary rocks by applying a pressure gradient assumed to be greater than the breakthrough pressure and then monitoring the pressure drop as flow occurred across the sample. The pressure at which flow ceased is therefore the breakthrough pressure and was found to fall between 0.1 and 4.9 MPa. Harrington et al. (2009) conducted step-wise increasing pressure experiments with nitrogen on the Sleipner caprock and found the initial breakthrough pressure to be 3.1 MPa. However, after flow was achieved the pressure dropped to 1.6–1.9 MPa. Skurtveit et al. (2012) conducted similar experiments but with CO_2 and found breakthrough pressure on a North Sea shale to range from 3.5 to 4.3 MPa.

From percolation theory the percolation threshold is the minimum porosity at which a connected pathway across a porous medium will form. If we assume that organic matter is CO_2-wet then we can consider the distribution of organic matter in a shale as the pores in percolation theory. In this context, the percolation threshold is the minimum concentration of organic matter which would create a connected path of organic matter pores across a shale layer. Percolation theory predicts that in a randomly distributed porous medium this threshold is met at approximately 12% (Larson et al., 1981). However, the laminated nature of organic matter in shales, like the Barnett, mean the percolation threshold may be lower in the direction of the laminations and higher across the laminations. This is confirmed by percolation theory in anisotropic materials (Lucena et al., 2003; Masihi et al., 2006; Sadeghnejad et al., 2010).

In addition, shales are often fractured and the fracture openings can effectively behave as larger pore-throats at a large scale. The ability for these fractures to transmit CO_2 through a caprock is, therefore, partially controlled by the wettability of the rock. A second barrier to contain buoyant CO_2 is the effect of friction and viscous forces which can be quantified in terms of rock permeability, relative permeability to CO_2, caprock thickness and the corresponding total head gradient (Downey, 1984; Espinoza, 2011).

1.2. Recent wettability studies

Until recently, our understanding of the wettability of shale with respect to s-CO_2 and brine was limited to studies on analogous minerals. Mica, a clay mineral and a component of clay sediment, is typically used to represent shale. Mica has a large flat crystal structure which makes it well suited for wettability studies (Iglauer et al., 2015a). Yet, there is little agreement in contact angle measurements of s-CO_2 and brine on mica (Broseta et al., 2012; Chiquet et al., 2007; Farokhpoor et al., 2013; Mills et al., 2011; Wang et al., 2013). Additionally, studies on quartz, an analog for tectosilicates, are also inconclusive with contact angles reported in the literature varying between 7° and 92° (Bikkina, 2011; Espinoza and Santamarina, 2010; Farokhpoor et al., 2013; Jung and Wan, 2012; Mills et al., 2011; Wang et al., 2013). Contamination and differing sample preparation during previous wetting experiments is likely the cause of the disagreement in the literature on the contact angle for quartz and mica (Iglauer et al., 2014). Given the uncertainty in contact angle measurements and the fact that clays and shales have been shown to become mixed-wet when exposed to crude oil (Borysenko et al., 2009), the need to understand the wetting of shale caprocks is important for CO_2 geological storage. An alternative approach is to measure directly capillary pressure on rock samples (Tokunaga et al., 2013). If conditions exist at which shale becomes CO_2-wet, then these rocks may facilitate the migration of CO_2 out of the reservoir and into overlying aquifers or escape back into the atmosphere.

Recent investigations into the wettability of a non-organic shale/s-CO_2/brine system found shale to be water-wet, as expected (Shojai Kaveh et al., 2016). The authors determined that there is a “low possibility of capillary breakthrough of CO_2 from silty shale caprocks”. Iglauer et al. (2015b) also investigated the effect of pressure on the wetting of a non-organic shale/s-CO_2/brine system but found that it approached mixed wet at higher pressures. Two individual shale wetting results have been reported on an organic shale and showed s-CO_2 to be water-wet (but approaching mixed wet) with a contact angle of 62° and 59° at 0.1 MPa–25 °C and 22.8 MPa–71 °C, respectively (Chaudhary et al., 2015).

Recent molecular dynamic simulations indicate that oil wetting on organic matter may increase as a function of thermal maturity with organic material becoming oil-wet as maturity increases (Hu et al., 2016). It has also been shown that organic shale may be oil-wet when exposed to hydrocarbons (Lan et al., 2015). These results are concerning because CO_2 storage projects may use an organic shale as a caprock. Also, depleted oil and gas reservoirs are promising locations due to their proven ability to trap hydrocarbons and the presence of necessary infrastructure for CO_2 transport and injection. CO_2 spontaneous imbibition in shales may be detrimental to capillary entry pressure of organic shale caprocks, such as, the Longyearbyen CO_2 storage project in Svalbard, Norway (Bohloli et al., 2014), and the SACROC Nothern Platform (Han et al., 2010). On the other hand, spontaneous imbibition of CO_2 in organic pores could be advantageous to CO_2 sequestration in the pore space of shales themselves through capillary trapping and sorption mechanisms (Busch et al., 2016).

In this paper we investigate the effect of total organic carbon (TOC) as well as organic thermal maturity, represented by vitrinite reflectance (R_o), on the contact angle of a brine/s-CO_2/shale system. We first introduce the samples selected and their preparation. Next, we discuss the recently developed methodology for determining contact angles in opaque capillaries and briefly describe the algorithm used to measure the contact angles. Finally, we present our results, compare our results to previous measurements in the literature, and discuss the implications for CO_2 storage. The over-all goal of this work is to evaluate the potential of structural CO_2 trapping capacity in geological formations capped by an organic-rich shale caprock.

2. Methods

2.1. Shale samples

To investigate the wetting of CO_2 on organic shales we used samples from the Barnett Shale. The Barnett Shale is a siliceous organic shale composed primarily of clay to silt-size quartz, illite, and, carbonate, with a minor amount of smectite type clays, pyrite, and phosphates (Loucks and Ruppel, 2007). Vitrinite reflectance values generally increase with depth; however the highest R_o values are found in the west where the formation was heated by Tertiary aged intrusives (Kinley et al., 2008). The organic content is highest in the clay rich intervals of the Barnett and typically ranges from 3 and 13% (Montgomery et al., 2005). The kerogen in the Barnett is a marine Type II kerogen with 95–100% amorphous organic matter (Jarvie et al., 2007).