



Adsorption of methane and carbon dioxide on gas shale and pure mineral samples



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ABSTRACT

We have measured methane and carbon dioxide adsorption isotherms at 40 °C on gas shale samples from the Barnett, Eagle Ford, Marcellus and Montney reservoirs. Carbon dioxide isotherms were included to assess its potential for preferential adsorption, with implications for its use as a fracturing fluid and/or storage in depleted shale reservoirs. To better understand how the individual mineral constituents that comprise shales contribute to adsorption, measurements were made on samples of pure carbon, illite and kaolinite as well. We were able to successfully fit all adsorption data for both gases in accordance with a Langmuir isotherm model. Our results show carbon dioxide to have approximately 2–3 times the adsorptive capacity of methane in both the pure mineral constituents and actual shale samples. In addition to obvious microstructural and compositional differences between real rocks and pure minerals, we hypothesize that water adsorption plays an important role in regulating surface area availability for other molecules to adsorb. The resultant volumetric swelling strain was also measured as a function of pressure/adsorption. We observe both clay and pure carbon to swell an amount that is approximately linearly proportional to the amount of adsorption.

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Introduction

Gas shales are complex rocks, characterized by heterogeneity in composition and structure at all scales. Similarly, the production of natural gas from shales is controlled by phenomena acting at many different scales, as has been reviewed by several authors (Bustin et al., 2008; Loucks et al., 2009; Wang and Reed, 2009; Sondergeld et al., 2010). One potentially significant property impacting production from these reservoirs is the adsorption of methane, which is controlled by the composition and microstructure of the rock. By storing gas in a dense, liquid-like adsorbed phase, the overall storage capacity of the rock is enhanced relative to if there were a free phase alone. Moreover, the release of this adsorbed phase is pressure dependent. As a reservoir is depleted, the adsorbed phase is freed, providing not just additional gas for production but helping to sustain pressure (and perhaps open pore throats for fluid flow) as well. While adsorption allows for larger quantities of gas to be in place and possibly produced, factors such as desorption pressure, kinetics, and alteration of effective stresses makes it difficult to know if desorbed gas will contribute significantly to production.

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In an effort to better understand the role of adsorption on production from gas shales, numerous authors have made valuable contributions to the literature through laboratory studies over the last 25 years. Schettler et al. (1991) performed experiments on pure clay, carbon and quartz minerals in addition to Devonian shales in an attempt to shed light on some of the factors affecting adsorption. They noted the significant adsorptive capacity of all of these minerals when measured individually. In addition, they found some cases in which the shape of the shale adsorption isotherm was best explained by adsorption on carbon (a proxy for kerogen), while others were better explained by illite adsorption. Similarly, Lu et al. (1995) measured the adsorptive capacity of several Devonian shale samples and pure illite. They concluded that while total organic content (TOC) played a first order role in the adsorptive capacity of their samples, illite was also responsible for significant gas storage, particularly in samples with little TOC.

More recent efforts have reached quite similar conclusions to previous studies. Ross and Bustin (2009) performed a laboratory investigation of the impact of composition and pore structure on total storage capacity in gas shales. In addition to carbon, they measured significant microporosity in clay minerals, particularly illite and montmorillonite. Chalmers and Bustin (2008) studied the impact of kerogen type and other geochemical properties on adsorption. They found that types I, II and III kerogen are all capable

of equally significant amounts of adsorption, but for differing reasons. Furthermore, they highlighted complexities associated with water content competing with adsorption sites in some cases (but not others) depending on geochemical composition and pore structure.

In addition to methane, there have been several studies highlighting the adsorptive capacity of carbon dioxide in gas shales. Nuttall et al. (2005) measured CH₄ and CO₂ adsorption on Devonian black shales in order to assess the potential for enhanced recovery or sequestration. They found CO₂ to have a adsorption capacity approximately 5 times greater than that of CH₄. Similarly, Kang et al. (2010) studied the adsorption of both gases on two samples from the Barnett shale, finding CO₂ to adsorb 5–10 times more than CH₄.

While ubiquitous in the coalbed methane literature, there is very limited data available to predict the accompanying volumetric strain caused by desorption during production or adsorption during gas injection. Lin et al. (2007) measured volumetric swelling strain resulting from adsorption of N₂, CH₄ and CO₂ in coal samples. They found roughly a linear relationship between swelling strain and adsorption. Similarly, Hol et al. (2011) studied the link between adsorption, swelling and stress in coal. Their results also show a linear relationship between adsorption and swelling. Moreover, they demonstrate the quantity of adsorption/desorption at a given pressure to be significantly influenced by the magnitude of external stress on the rock. Several authors have suggested the potential importance of adsorption-induced deformation in the context of gas shales (Cui et al., 2009; Ross and Bustin, 2007), however, no efforts have directly addressed the topic to date.

In this study, we extend these previous works and investigate the adsorption of CH₄ and CO₂ on various shale and pure mineral samples in the laboratory. Samples from four different formations were studied, as well as pure carbon, illite and kaolinite. Using the methods described below, we measured the adsorption of CH₄ and CO₂ on both shale samples and pure minerals. In a triaxial apparatus, the resultant volumetric swelling strain associated with adsorption is measured. Our overall objective is to further the effort toward understanding adsorption in gas shales. In addition, the experimental results are analyzed and discussed in the context of production from gas shales.

Sample description

Experiments were first carried out on pure carbon and clay materials. Activated carbon (Filtrisorb 400, 12 × 40 mesh) was purchased from Calgon Carbon to be representative of mature kerogen. Kaolinite and illite samples were obtained from the Clay Mineral Society and sold to us as pure clay samples. Both CH₄ and CO₂ adsorption isotherms were measured for each of these materials. Following these experiments, the adsorption of CH₄ and CO₂ was measured on gas shale samples from the Barnett, Marcellus, Eagle Ford and Montney reservoirs. To the degree possible, samples of representative mineralogical composition were selected from each of these shales. The Barnett sample was highest in TOC (>5%) and had a relatively high clay content (37.4%) as well. The Montney sample and Eagle Ford samples had a similar amount of TOC (2.0% and 1.8%, respectively), but the Montney sample had much more clay and quartz whereas the Eagle Ford was mostly carbonate (>70%). The Marcellus sample was lowest in TOC (1.2%) and had the highest amount of clay (~50%). A complete description of the mineralogy of these samples is provided in Table 1.

In addition to mineralogy, Rock Eval Pyrolysis data was gathered on three of the four samples. This data is also presented in tabulated format in Table 1. Rock Eval Pyrolysis involves heating a small amount of ground up sample at a constant rate (5 °C/min, in this

Table 1

Sample mineralogy and Rock Eval Pyrolysis data. Pyrolysis data indicates that the Eagle Ford 127 sample lies within the dry gas window, while the Barnett and Marcellus samples are less mature and slightly more oil-prone.

| | Barnett 31 | Eagle Ford 127 | Marcellus | Montney |
|--------------------------------|------------|----------------|-----------|---------|
| Depth (ft) | 8640.8 | 12,771.35 | 6300 | 7614.52 |
| Depth (m) | 2633.7 | 3893.70 | 1920.73 | 2321.50 |
| Initial Mass (g) | 41.32 | 46.46 | 34.42 | 38.33 |
| Mass After Drying (g) | 41.19 | 46.35 | 34.34 | 38.22 |
| Water by Mass% | 0.31 | 0.24 | 0.22 | 0.28 |
| TOC (%) | 5.3 | 1.8 | 1.2 | 2.0 |
| Quartz (%) | 51.3 | 7.0 | 38.0 | 42.3 |
| Plagioclase/Feldspar (%) | 4.0 | 4.0 | 6.0 | 11.9 |
| Calcite (%) | 0.0 | 80.0 | 1.0 | 8.1 |
| Dolomite (%) | 0.4 | 1.0 | 1.0 | 9.9 |
| Pyrite (%) | 1.7 | 1.0 | 1.0 | 3.5 |
| Apatite (%) | 0.0 | 2.0 | 1.0 | 0.0 |
| Total Clay (%) | 37.4 | 5.0 | 52.0 | 24.1 |
| S1 (mg HC/g rock) | 4.4 | 2.88 | 2.06 | N/A |
| S2 (mg HC/g rock) | 6.1 | 1.36 | 5.15 | N/A |
| S3 (mg HC/g rock) | 0.3 | 0.54 | 0.31 | N/A |
| Tmax (°C) | 452 | 466 | 369 | N/A |
| HI (mg HC/g TOC) | 115 | 75 | 439 | N/A |
| OI (mg CO ₂ /g TOC) | 6 | 30 | 26 | N/A |

case), and measuring the hydrocarbons produced from the sample as a function of temperature. The S1 and S2 peaks quantify the amount of hydrocarbon thermally extracted at approximately 300 °C and 550 °C, respectively. S1 essentially indicates that amount of free hydrocarbons (gas or oil) present in the sample, while S2 is a better indication of hydrocarbon generation potential upon further heating and burial. S3 quantifies the amount of CO₂ relieved from the organic matter during pyrolysis of kerogen, and is indicative of the amount of oxygen in the kerogen. The Tmax temperature indicates that temperature at which the S2 peak reaches a maximum, which serves as an indication of the maturation stage of the organic matter. The hydrogen index (HI) and oxygen index (OI) can be calculated from this data, and are typically used to characterize the origin of the organic matter. All of this information can be combined to delineate whether the sample lies within the immature, oil, condensate or dry gas window (Peters and Moldowan, 1993). Of the three samples tested, only one lies conclusively within the dry gas window (Eagle Ford 127). The Barnett 31 and Marcellus samples lie within the condensate and late-oil windows, respectively.

Methodology & background

Adsorption measurements

The adsorptive potential for a material is quantified by measuring the surface uptake of an adsorbate over a series of pressures at constant temperature, defining what is called an adsorption isotherm. In addition to describing adsorptive capacity, the magnitude and shape of the isotherm gives insight into pore structure and surface properties of the material. In general, the more surface area and the stronger the adsorbate–adsorbent interaction energy, the greater the amount of adsorption. However, pore size distribution also plays an important role. As pores become smaller and smaller, molecules residing within such pores become increasingly more impacted by the enclosing surfaces on all sides. In other words, the interaction energy from multiple surfaces coalesce, resulting in an overall increase in attraction relative to a free surface. Thus, materials with a large micropore volume are generally very adsorptive. When performing calculations or making inferences about pore structure and surface area from adsorption

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