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The dynamics of hydraulic fracture water confined in nano-pores in shale reservoirs

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ABSTRACT

Hydraulic fracturing treatments and horizontal well technology are central to the success of unconventional oil and gas development. In spite of this success, replicated over several thousand wells over diverse shale plays, hydraulic fracturing for shale wells remains poorly understood. This includes the poor recovery of hydraulic fracture water, the inability to explain the progressive increases in produced water salinity and an incomplete understanding of the potential trapping mechanisms for hydraulic fracture water.

In this work, we focus on describing the distribution of saline water in organic and inorganic pores as a function of pore size and pore morphology with the purpose of providing fundamental insights into above questions. A kerogen model is constructed by mimicking the maturation process in a molecular dynamics simulator and it incorporates structural features observed in SEM images including the surface roughness, tortuous paths, material disorder and imperfect pore openings of kerogen pores. This work also extends this kerogen model through the use of oxygenated functional groups to study fluid behavior in partially mature shales associated with non-zero oxygen to carbon ratios.

Our results demonstrate that water entrapment mechanism and the distribution of water and ions in organic and inorganic pores are strongly related to the pore-surface mineralogy and pore width. The work in this paper also underscores the importance of kerogen thermal maturity and pore roughness on the accessibility of the kerogen material to water.

Introduction

For shale formations characterized by extremely low permeability, hydraulic fracturing treatments combined with horizontal well completions are widely utilized to enhance well productivity. The fluid employed for hydraulic fracture treatments, commonly referred to as hydraulic fracture water, largely comprises of water with other viscosity-reducing agents. One of the key observations related to hydraulic fracture stimulation is the low recovery of hydraulic fracture water during well clean-up and flowback operations. King (2012) reported that for the Haynesville shale, only 5% of the stimulation fluid was reported as recovered while for the Barnett and Marcellus shale, the percentage recovery of fracture water was closer to 50%. Produced water salinity has also been observed to increase with time and King (2010) reported that salt concentration in produced water may approach 80,000–100,000 ppm at later times even with fairly fresh water employed for stimulation treatments. At this time, there is a poor understanding of the fate of hydraulic fracture water and its interactions with the organic and inorganic nanopores that characterize shales. It is likely that the distribution of fracture water during post-stimulation may impact well productivity, and therefore, understanding the dynamics of hydraulic fracture water in shale may be beneficial to design more optimal hydraulic fracturing procedures to enhance well performance and hydrocarbon recovery.

Some theoretical research has been proposed to account for the low recovery phenomenon of hydraulic fracture water from macroscopic perspectives. The clay minerals in inorganic material are generally considered to be water-wetting (Elijah, 2011) and may cause irreversible water adsorption (King, 2012). Additionally, when shales are exposed to hydraulic fracture water, capillary forces (Sondhi, 2011) and the mixed wettability of shales (Elijah, 2011) may lead to the counter-current imbibition of water (Qin, 2007). King (2012) also reported that hydraulic fracture water may be trapped in micro-fractures and small pores created by pressure release. Michel and Civan (2012) attributed the entrapment of hydraulic fracture water to capillary non-equilibrium

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effects. However, these theories remain untested and the pore-scale phenomena controlling the distribution of fracture water are still poorly understood.

Recent research has also revealed that the microstructure of shales can be highly complex with a high degree of heterogeneity. The utilization of focused ion beam-SEM methods (Curtis et al., 2011; Chalmers et al., 2012) and other approaches such as mercury injection capillary pressure experiments (Sondergeld et al., 2010) demonstrated that shales are characterized by pores that are typically sub-100 nm in diameter forming complex pore networks whose connectivity is poorly understood. Additionally, the organic kerogen material has been shown to have a sponge-like internal structure with a substantial percentage of the pore volume contained in nano-sized pores (Curtis et al., 2011). The behavior of fluids in these nanoporous media is therefore not very well known primarily because of a lack of practical experimental approaches to probe pore volumes associated with these nanoscale pores. This work relies on the use of microscopic virtual experiments, molecular dynamics simulations, to understand fluid distribution in shale nanopores and to identify the factors governing this distribution specifically for hydraulic fracturing fluids.

Traditionally, the model chosen as a proxy for organic pore systems is based on the graphene slit pore model that has been used to determine the thermodynamic properties of adsorbed fluids in porous kerogen (Müller and Hung, 2000; Severson and ad Snurr, 2007; Diaz-Campos, 2010; Didar, 2012; Liu and Wilcox, 2012a,b; Mosher et al., 2013). Graphene slit pores have been utilized in Severson and ad Snurr (2007) to evaluate the effect of temperature, pressure, pore width and alkane chain length on adsorption of various single component alkanes, while Diaz-Campos (2010) and Didar (2012) evaluated gas sorption and gas solubility in water in nanoscale graphene slit pores. Mosher et al. (2013) also investigated methane adsorption in micro- and meso-scale pores modeled by the pure graphite slit pore model. A few studies (Müller and Hung, 2000; Liu and Wilcox, 2012a,b) involving the use of activated carbon models that contain surface-bound oxygenated groups in modified graphene slit pore models focused on the behavior of fluid molecules in the vicinity of activated carbon and demonstrated that fluid behavior may be significantly different from the observations obtained for pure graphene surfaces. Müller and Hung (2000) investigated the adsorption of water and water vapor–methane mixture on activated carbon pores, while in more recent work, Liu and Wilcox (2012a,b) analyzed CO_2 adsorption in micro- and meso-sized slit pores with functionalized graphitic surfaces.

However, the smooth, planar and perfect surface of the graphene slit pore model may not be able to represent the complexity in kerogen including surface functionalized chemistry, pore surface roughness, and tortuosity of the pore networks. Consequently, more realistic kerogen models have recently been employed to study the material order to emphasize the dominant role of pore morphology on fluids behavior (Firouzi and Wilcox, 2012; Hu et al., 2013). In Firouzi and Wilcox (2012), a pure carbon-based 3-D pore network using the Voronoi tessellation method was utilized to analyze the transport and storage of CO_2 in this material. In a previous study, Hu et al. (2013) employed a simplified inactivated porous kerogen model constructed by simulating the high pressure and temperature effects under which the organic matter was formed to study the confinement of aqueous water and illustrated significantly different mechanisms of water entrapment in small pores arising solely out of complex pore geometries. The model of Hu et al. (2013) was constructed by mimicking the maturation process leading to kerogen formation. However, the work in Firouzi and Wilcox (2012) and Hu et al. (2013) are restricted to highly mature kerogen characterized by very low oxygen-carbon ratios (Vandenbroucke and Largeau, 2007). Because the thermal maturity of kerogen is linked to the O/C and H/C ratios, this study extends the work of Hu et al. (2013) and incorporates representative oxygenated groups in activated kerogen models to model organic kerogen pores of varying degrees of maturity.

In this paper, the activated kerogen model is utilized to study the behavior of brine in organic shale nanopores while a magnesium oxide slit pore is employed as a proxy for inorganic shale nanopores. The impact of pore width and pore morphology on water entrapment in organic and inorganic shale nanopores is also investigated in this study. The activated kerogen model considered in this work incorporates some major structural properties of the kerogen such as surface roughness, tortuous paths, material disorder and pore imperfections. Our results indicate that kerogen of intermediate maturity may have heterogeneous wettability and therefore may contain water and is consistent with some recent experimental work demonstrating the presence of water in kerogen (Chalmers and Bustin, 2010; Ruppert et al., 2013). In Chalmers and Bustin (2010), moisture contents ranging from 0.5% to 15% were detected in various samples from Devonian, Jurassic and Cretaceous shales with varying degrees of kerogen maturity degrees from immature to highly mature samples. They also indicated the potential impact of the presence of moisture in kerogen on hydrocarbon sorption capacity depending on the distribution of hydrophilic and hydrophobic sites throughout the pore networks. Ruppert et al. (2013) combined small-angle neutron scattering and ultrasmall-angle neutron scattering to investigate Barnett Shale samples. In Ruppert et al. (2013), the pore accessibility to both water and methane over a wide size range of pores was demonstrated, and most pores in the studied Barnett samples were shown to be contained in the organic components. Therefore our study provides a strong theoretical rationale for these observations. We demonstrate the role of pore surface mineralogy, surface roughness and the kerogen maturation on the brine water behavior and explain the possible physiochemical mechanisms behind the water entrapment. The work is a fundamental study and is valuable for a better understanding of hydraulic fracture water and dissolved ion distributions, water loss and high produced water salinity related to hydraulic fracturing.

Shale modeling

Organic matter modeling

The organic matter in shale, known as kerogen, is a mixture of insoluble macromolecules with a highly complex chemical composition that cannot be described by a single formula. Kerogen typically forms from dead organisms buried at sufficiently high pressures and temperatures for prolonged geologic time periods. As kerogen evolves during maturation, the functionalized molecules and mobile hydrocarbons may be lost, resulting in a decrease in total molecular weight as well as a reduction in H/C and O/C atomic ratios (Vandenbroucke and Largeau, 2007). The compositional changes are usually illustrated using a van Krevelen diagram where H/C and O/C atomic ratios are used as indicators of rock maturity (Tissot and Welte, 1978).

To reflect these changes in kerogen maturity, the inactivated kerogen model of Hu et al. (2013) is extended through the use of oxygenated functional groups in this work. The pure carbon-based kerogen model in Hu et al. (2013) was systematically constructed using graphene segments by running molecular simulations under very high pressure (7252 psi) and temperature (1340 °F) for a sufficiently long time to mimic the thermal evolution process under which kerogen is formed. In this work, we chose the carbonyl ($-C{=}O$) group as a representative oxygenated group whose stability on graphene or graphite surfaces has been established and