A USANS/GP-SANS Study of the Accessibility of Pores in Gas Shale to Methane, Water, and Brine

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Gas shale formations are an increasingly important source of natural gas with the advent of innovative hydrofracturing and horizontal drilling techniques. However, the efficiency of methane production from gas shale can be affected by the percentage of closed versus open network pores. Some investigations of closed porosity in shale are available, but the interpretations are hampered because porosity has been measured on dry samples and in situ shale is wet. Shale can contain minerals that swell in water and methane mobility may be less than measured in dry samples. In addition, shale is often brine-rich and brine is known to affect mineral swelling differently from pure water. In a pilot study of the accessibility of methane in wet shale, we have studied the penetrability of methane, water, and brine solution into Mississippian Barnett Shale samples using the ultra-high-resolution small-angle neutron scattering (USANS) diffractometer at the National Institute of Standards and Technology and the General Purpose Small-Angle Neutron Scattering Diffractometer (GP-SANS) at Oak Ridge National Laboratory. Neutron scattering techniques are useful in this regard because they can be used to determine pore size distribution of materials from the nanometer to micron sizes. The two instruments are complementary as USANS and GP-SANS are configured to examine pores between 10 to 0.1µm and 0.1 µm to 0.5 nm in size, respectively.

In a recent extension of neutron scattering, Melnichenko et al., have developed a technique to determine the fraction of pores over these size intervals that are inaccessible to fluids such as CH₄ and H₂O. At the correct conditions only scattering from closed pores is observed. The conditions for our samples were 10,000 psi CD₄ for the methane measurement and 75%D₂O/25% H₂O for the water and brine measurements. By comparing scattering from closed pores to that of all pores, the fraction of inaccessible pores can be obtained over the full size range as a function of pore sizes.
Two Barnett Shale butt core samples were chosen for analyses because they had very different measured porosities (1.56% and 6.28% for samples 72 and 152, respectively). Crushed samples and thin (~0.8x16 µm) wafers were cut parallel to bedding from both samples. The wafers were oven dried at 60°C for one week and were soaked in solutions of 1) 75% D$_2$O, 2) 75% D$_2$O/brine, 3) 65% D$_2$O, and 4) 65% D$_2$O/brine for at least two weeks (brine composition = 200,000 ppm NaCl). Sample runs included 1) dry samples run at ambient conditions (ac), 2) dry, pressurized (10,000 psi) CD$_4$ samples, and 3) samples soaked in 75% D$_2$O (ac) and 75% D$_2$O/brine (ac).

GP-SANS data are currently being reduced and interpreted but preliminary evaluation of the USANS runs shows that

1. There is substantial penetration by both CD$_4$ and D$_2$O at all scales, but there are pores inaccessible to D$_2$O and CD$_4$ even on the largest scale examined (10 µm).
2. Porosity variations in mm-sized sub-samples are large (factor of 2).
3. Crushing the shale modifies the larger scale porosity substantially and should not be used.
4. Brine impacts appear to be relatively small.