

A New Core Measurement Methodology to Quantify Total Gas Storage

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The storage of gas in organic shales occurs both as a sorbed phase mainly adsorbed on the surface of the organic materials and/or absorbed in the organic material, and as free gas in pore space. The standard method to measure the total storage is to make two separate measurements. The first is a measurement of the sorbed gas storage done on crushed samples at reservoir temperature, and the second is a standard low-pressure helium pycnometer measurement again done on crushed samples. Total storage is then taken as the sum of the two measurements. This procedure although relatively rapid and inexpensive has a variety of issues associated with it.

Nanometer scale SEM images have shown that in some organic shale systems a large percentage of the pore space that stores gas is made up of pores in the organic material. These pores have sizes on the one to ten nanometer scale. For pores of this size the volume occupied by the adsorbed phase significantly reduces the volume available for the free gas phase. In some cases pore throats may be completely blocked by the adsorbed phase so that the free gas cannot enter the larger pore body. Different gases adsorb different amounts. For organic shales helium adsorbs very little, methane considerably more and carbon dioxide adsorbs more than methane. This implies that total storage cannot just be a linear sum of the amount of the adsorbed methane and the amount of free gas as measured by helium.

The amount of adsorption is a strong function of pressure and a weak function of temperature. As such the storage curve must be constructed from measurements at the initial reservoir pressure and at a range of lower pressures to provide storage as the reservoir is drawn down. Ideally it would be measured at reservoir temperature.

Organic shale is a very complex heterogeneous system the components of which include materials of widely varying elastic properties. Moreover pore shapes can also be very variable. As such pore volume can be a very complex function of confining pressure and pore pressure. It is even possible that the simple concept of effective pressure will break down as the organics may not be stress supporting. This also requires measurements made at the appropriate reservoir pressure and appropriate pore pressure. Measurements on crushed samples cannot accommodate these requirements.

The authors have developed and tested a new methodology to measure total storage as a function of pore pressure and then to model the storage curve in terms of an adsorbed component and a free gas component. Measurements have been done on organic shale reservoir rocks using helium, methane, carbon dioxide, and binary mixtures of the latter two.

The storage measurement is done on a cylindrical plug taken from a core. It is essentially a high-pressure pycnometer measurement in which the sample is sleeved and under confining pressure. The measurement starts with the sample at an initial pore pressure. A valve to a gas reservoir of known volume and higher pressure is then opened and the pressure allowed to equilibrate to a final pressure. The gas stored in the sample by raising the pore pressure from the initial pressure to the final is calculated from mass balance using the known volume of the reservoir, the dead volumes, and the gas equation of state. Repeating this procedure for multiple pressure points provides the desired total storage curve.

The total storage curve is then modeled to extract the adsorbed and free gas as a function of pressure. To model the curve it has been assumed that the sorbed gas can be modeled by a Langmuir adsorption isotherm. This is the assumption that is generally made in the standard sorption measurements and provides a good fit to the data. With that assumption the storage curve is modeled

by five parameters: the Langmuir pressure P_L , the moles of adsorbed gas at infinite pressure S_{amax} , the density of the adsorbed state ρ_a , the pore volume at zero pore pressure V_{p0} , and the pore volume compressibility C_p .

The figure below shows an example of a methane storage curve for a organic shale sample, and a model curve that fits the data. With the exception of the last pressure point the model is an excellent fit to the measured data.

One systematic error in this measurement procedure is pore volume in stress relief cracks. NMR measurements on the samples when saturated with methane at high pressure can provide the volume of these cracks as a function of pressure. Typically this volume represents about 0.5% porosity.

