Laboratory characterization of shale pores

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Abstract. To estimate the potential of shale gas reservoir, one needs to understand the characteristics of pore structures. Characterization of shale gas reservoir microstructure is still a challenge due to ultra-fine grained micro-fabric and micro level heterogeneity of these sedimentary rocks. The sample used in the analysis is a small portion of any reservoir. Thus, each measurement technique has a different result. It raises the question which methods are suitable for characterizing pore shale. The goal of this paper is to summarize some of the microstructure analysis tools of shale rock to get near-real results. The two analyzing pore structure methods are indirect measurement (MIP, He, NMR, LTNA) and direct observation (SEM, TEM, Xray CT). Shale rocks have a high heterogeneity; thus, it needs multiscale quantification techniques to understand their pore structures. To describe the complex pore system of shale, several measurement techniques are needed to characterize the surface area and pore size distribution (LTNA, MIP), shapes, size and distribution of pore (FIB-SEM, TEM, Xray CT), and total porosity (He pycnometer, NMR). The choice of techniques and methods should take into account the purpose of the analysis and also the time and budget.

1. Introduction

Characterization of pore structure is important in gas exploration to estimate Original Gas in Place and the flow structure of gas shale reservoirs [1]. Like other unconventional hydrocarbons, shale gas production is affected by permeability. Its permeability is influenced by pore-dominated microstructures. Thus, an understanding of pore distribution is the key to identify shale behavior. Identification of shale pore characteristics is hindered by the lack of tools to investigate their pore structure. Shale rock has a variety of degrees of diagenesis and consists of shales, mudstones, limestones, dolomite, porcellanites, and sandstone; therefore, the pore structure of shale rock in different basins will be difficult to generalize. The kerogen organic matter and the shale particles have micropores range from nano to macropores. According to IUPAC (International Union of Pure and Applied Chemistry), pores are classified as micropores (<2 nm), mesopores (2- 50 nm), and macropores (> 50 nm). In this paper, we describe several state-of-the-art methods of characterizing microporous materials to provide recognition for the pore structure of gas shales reservoir. There are two analyzing pore structure methods, direct observation and indirect measurement [2].

2. Indirect Measurement

2.1. MIP (Mercury Injection Porosimetry)

MIP measurement is the standard method for characterizing pore throat size distribution in media that ranging from a micron to a nano-scale. MIP test measures the volume of mercury and pressure which is injected leading to a pore throat profile and a pore volume measurement [3]. However, for pore throats that measured less than 3 nm, MIP must be combined with an additional testing procedure because of the limitation of the maximum instrument pressure. The maximum pressure of MIP

instrument is 60.000 psi. According to Washburn's equation, a pressure of 60.000 psi can cause mercury to access pore as thick as 3 nm. NMR (Nuclear Magnetic Resonance) is commonly used to complement MIP because NMR can penetrate the residual porosity and interlayer.

MIP methods are a cheap source of initial investigation to have some understanding about the porosity of shale gas reservoir. MIP is an analysis which works without unique and time-consuming treatments. At low applied pressure, open surface pores do not saturate with mercury because of nonwetting nature of mercury. But due to a high applied pressure, the artificial cracks appear on shale's surface.

2.2. Helium Porosimetry

Helium is an inert nature gas, which has a tiny molecular diameter (0.260 nm) [3], so it can penetrate into tiny and opened-pores. This technique is reliable because it is not sensitive to any chemical reactions and it has the lowest adsorption trend on the grain and pore surface. Helium porosimetry values are more reflective of the effective porosity than values which is obtained by MIP because the helium has smaller diameter molecule than that of mercury [4]. Due to the low permeability of the shale samples, helium requires more time to equilibrate in the shale samples by diffusion than mercury.

Many factors can affect shale porosity measurement, i.e., adsorption effects, sample size, crushed sample weight, pore pressure net over-burden stress, and pore access problems to gas and liquid due to the low permeability of shale [5].

2.3. NMR (Nuclear Magnetic Resonance)

NMR measure responds to the hydrogen atoms in the pore space [3]. Examination of the entire pore network (size and distribution) works best using NMR and gas injection techniques [3]. NMR is a method of gaining information on pore space (size, shape, and volume) by quantifying the interactions of protons and the porous media. The NMR and MIP measurements indicate that NMR can characterize the pore bodies that are not being accessed by the mercury data [3].

2.4. Gas Adsorption

Low-temperature N_2 adsorption/desorption (LTNA) is used to calculate pore size distribution by utilizing capillary condensation according to the Kelvin Equation in pores. LTNA techniques are suitable for material examination that have fine pores that range from 2 nm to 300 nm, e.g., mudrocks and coals. The principle of this method is to calculate the remaining gas after it interacts with solid. These methods result in information of the textural properties of porous materials, for example, surface area and pore structure.

Either N_2 adsorption method or MIP method alone cannot provide a complete description of the actual pore-structure characteristics in shale sample because N2 adsorption method can be used to identify mesopores and MIP method can be used to mainly analyze micropores [6].

3. Direct Observation

Direct observation techniques are available to describe the nature of shale porosity in 2D or 3D images directly. They can represent the porous rock space; therefore, it can produce qualitative and quantitative data on shale rock porosity. Direct observation includes optical microscopy, scanning electron microscopy, transmission electron microscopy and X-ray tomography.

3.1. Optical microscopy /Thin section analysis

Optical microscopy is the most accurate and repeatable evaluation of the pore system of reservoir rock samples. To obtain pore system, texture, mineral constituent, diagenesis and reservoir quality of the sample, the polarizing microscope is used with magnification up to 40x. However, in spite of some information available (e.g., microtextures, microstructures and the mineralogical component of rock), the actual three-dimensional grain relationships cannot be visualized.

Transmitted and reflected light microscopy cannot image mesopores and micropores because of the low power of magnification (1000×). The connected-porosity of shale can be visualized by stacking some thin sections into datasets; therefore, they can be reconstructed into 3D. The mineral composition can also be detected directly. It takes a lot of thin sections to be reconstructed; consequently, it takes a long time.

3.2. SEM (Scanning Electron Magnetic)

SEM is one of direct observation that is used to investigate porosity and visualize in 2D image with a relatively low resolution [7]. Currently, the deficiency can be solved by the addition of an emission microscope field coupled with an ion milling device (i.e., FIB: Focused Ion Beam); thus, shale pore structures can display a volume of 3-dimensional specimens. FIB milling technique removes topographic features and produces flat surface [8]; hence, mesopore and micropore can be visualized. FIBSEM has pixel resolution about 1 nm; thus, the morphology of pore surfaces, single organic materials and minerals are relatively easy to recognize [9] because a grain size of the mineral is usually between 3.2-35 μm [10].

FE-SEM characterization method is able to capture a wider range of pore size than the technique which uses N_2 adsorption or MIP [6]; thus, FE-SEM provides a complete picture about the real pore size distribution of shale samples than N_2 adsorption or MIP.

Measurements of shale porosity using the SEM-FIB high-resolution 2D images technique result in large pore size, whereas the variation in pore size and shape with interconnectivity is not identified clearly. However, these techniques are expensive and time consuming which limiting the number of samples analyzed. This will affect the porosity estimation of shale rock as a shale gas reservoir.

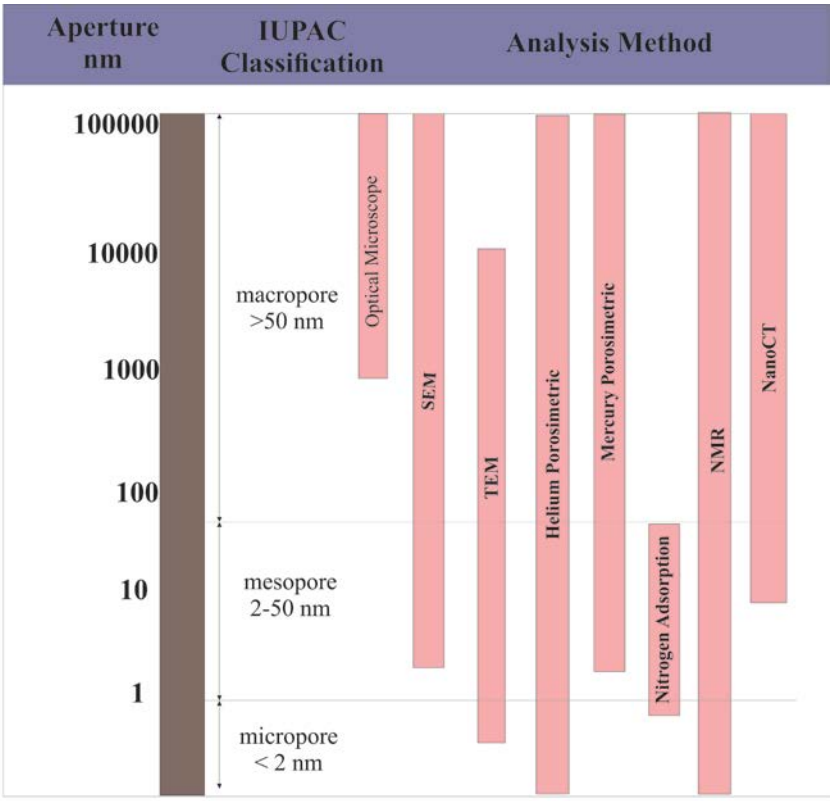

Figure 1. Various analytical methods/techniques use for estimating porosity and pore size distributions in unconventional gas reservoirs (modified from [14]).

3.3. TEM (Transmission electron microscopy)

TEM preparation sample uses FIB (Focused Ion Beam) milling to prepare such ultrathin sample because TEM are transmission techniques, which require the samples to be electron and X-ray transparent (thinner than 200-250 nm).

TEM analysis requires a high cost; therefore, the number of analysis performed on a sample is limited so that there are only fewer representatives to describe the pore structure of a shale gas reservoir. TEM provides spatially-resolved information on organic constituent texture in the sub-nanometer scale, so it is well-suited to the nanoscale characterization of shale gas reservoir.

3.4. X-Ray Computed Tomography

This technique, developed in recent years using X-ray in extensive, fast and nondestructive Omni-scanning of rock samples and scanning images, is finally used in the numerical reconstruction of 3D pore throat texture [11]. X-Ray CT can be applied in the microscale to nanoscale of rock samples of various sizes to obtain pore throat texture in a nanoscale, a microscale, and a milliscale; therefore, it is possible to position different pores and throats in samples [12]. Smaller samples and a shorter distance between source and detector produce higher resolution images of X-ray CT. X-ray CT, like standard medical CT scanning, can be used to visualize microstructures in a centimeter to millimeter scale in the shale. High-resolution micro-CT can be used to describe microstructures in a micrometer scale. Identified pores, otherwise determined by the resolution, are also affected by the threshold method used. Understanding the scanned characteristics of the sample is needed to determine the threshold method [13]. But we can visualize microstructure in a nanometer scale using nano-CT, in which the sample used is ~ 9 μm in diameter x 12 μm length.

4. Conclusions

Because of the wide range of pore size distribution, it requires multiple types of methods and multi-scale visualization. LTNA and MIP Porosities are not the same, and the result in each case is an average representation of a range of porosities evaluated in these two techniques. TEM and SEM/FIB are reliable techniques for free porosity visual evaluation, but both techniques require a very small sample, so the result is not representative. X-ray CT can show the pore structure in the rocks thoroughly; therefore, it will look like the original condition. The choice of techniques and methods should take into account the purpose of the analysis and also the time and budget.

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