Journal of Unconventional Oil and Gas Resources 8 (2014) 1–13

Contents lists available at ScienceDirect

Journal of Unconventional Oil and Gas Resources

journal homepage: www.elsevier.com/locate/juogr

Review

Comparisons of pore size distribution: A case from the Western Australian gas shale formations

Adnan Al Hinai [a,*], Reza Rezaee [a], Lionel Esteban [b], Mehdi Labani [a]

[a] Curtin University, Department of Petroleum Engineering, Level 6 ARRC, 26 Dick Perry Avenue, Technology Park West, Kensington, WA 6151, Australia
[b] CSIRO-ESRE, Petroleum and Geothermal Resources, 26 Dick Perry Avenue, Kensington, 6151 Perth, Western Australia, Australia

A R T I C L E   I N F O

Article history:
Received 3 March 2014
Revised 14 May 2014
Accepted 22 June 2014
Available online 27 July 2014

Keywords:
Gas shale
Mercury injection capillary pressure
Nuclear magnetic resonance
Pore size distribution
Transverse relaxation time
Nitrogen adsorption

A B S T R A C T

Pore structure of shale samples from Triassic Kockatea and Permian Carynginia formations in the Northern Perth Basin, Western Australia is characterized. Transport properties of a porous media are regulated by the topology and geometry of inter-connected pore spaces. Comparisons of three laboratory experiments are conducted on the same source of samples to assess such micro-, meso- and macro-porosity: Mercury Injection Capillary Pressure (MICP), low field Nuclear Magnetic Resonance (NMR) and nitrogen adsorption (N2). High resolution FIB/SEM image analysis is used to further support the experimental pore structure interpretations at sub-micron scale.

A dominating pore throat radius is found to be around 6 nm within a mesopore range based on MICP, with a common porosity around 3%. This relatively fast experiment offers the advantage to be reliable on well chips or cuttings up the pore throat sizes >2 nm. However, nitrogen adsorption method is capable to record pore sizes below 2 nm through the determination of the total pore volume from the quantity of vapour adsorbed at relative pressure. But the macro-porosity and part of the meso-porosity is damaged or even destroyed during the sample preparation.

BET specific surface area results usually show a narrow range of values from 5 to 10 m^2/g. Inconsistency was found in the pore size classification between MICP and N2 measurements mostly due to their individual lower- and upper-end pore size resolution limits. The water filled pores disclosed from NMR T_2 relaxation time were on average 30% larger than MICP tests. Evidence of artificial cracks generated from the water interactions with clays after re-saturation experiments could explain such porosity over-estimation. The computed pore body to pore throat ratio extracted from the Timur–Coates NMR model, calibrated against gas permeability experiments, revealed that such pore geometry directly control the permeability while the porosity and pore size distribution remain similar between different shale gas formations and/or within the same formation. The combination of pore size distribution obtained from MICP, N2 and NMR seems appropriate to fully cover the range of pore size from shale gas and overcome the individual method limits.

Contents

* Corresponding author.
E-mail address: Adnan.al-hinai@postgrad.curtin.edu.au (A.A. Hinai).

http://dx.doi.org/10.1016/j.juogr.2014.06.002
2213-3976/

1. Introduction

While most of the clay-rich rocks, or shales, represent large volumes of petroliferous geological systems, they often act as sealed hydrocarbon accumulations and/or source rocks, and/or in some cases as a hydrocarbon reservoir in itself. Such multi-characters are often associated with their very low permeability (nanoDarcy range) and diagenetic history. The complexity of the pore structure and the clay types will then control the ability of shales to act as a barrier–source–reservoir, that is, will determine their capacity to flow and trap fluids.

Shales have a unique pore structure, due to different geological histories that overlay complex structures, as well as variant sedimentology and diagenetic processes (Bustin et al., 2008; Evdokimov et al., 2006) that play at various scales from the nano- to macro-scale, making such reservoirs challenging to understand (Curtis et al., 2010). Shale's low porosity combined with ultra-low permeability has led to poor and difficult experimental core analysis practice (Luffel, 1993; Washburn and Birdwell, 2013).

Transport properties of gas shale are attributed to fractures and matrix permeability. Fracture permeability relates to fast fluid displacement through a rock volume. Such transport in gas shales is usually induced (hydraulic) fracture to produce gas from the formation, and rarely inherited, dominated by Darcy law. Matrix permeability corresponds to slow fluid motion through the very low permeability of gas shale that is mostly dependant on the distribution and geometry of the pores. Such transport is dominated by diffusion and capillary force mechanisms. At this stage, the only way to extract gas from gas shale is through extensive hydraulic fracturing (Gale et al., 2007) from which the gas recovery efficiency will depend on the matrix permeability to refill the fracture and matrix fluid storage or trap properties of the gas shale. This study will only focus on the slow transport aspects by investigating the pore characteristics and their distribution through two gas shale formations from the Perth Basin, combining four state of the art methods capable to handle challenging small scale of investigation (nanoscale).

The pore space can be regarded as the connection of the void pore bodies connected by smaller void conduits (pore throats). Such characteristics can be described through geometrical rock properties including porosity, size, shape and distribution of pore bodies and throats, pore connectivity and body-to pore throat size ratio. Of course, a fluid's capacity to flow through the pore network (hydraulic conductivity and permeability) will also depend on the fluid–solid interactions, tortuosity of the pore network, intrinsic structures such as veins, faults or bedding (i.e. heterogeneities) and anisotropic aspects of these characteristics. It is therefore crucial to understand the pore structures of shale gas.

To assess the small Pore Size Distribution (PSD) of shale gas, a limited range of laboratory techniques can be applied, with respective pros and cons, but together they give a quite reasonable PSD overview to overcome these limitations. The techniques are as follows.

(1) Mercury Injection Capillary Pressure method (MICP) is the most common method to characterize the pore throat size distribution, using injection of mercury under controlled pressure.
(2) Nitrogen adsorption (N_2) method evaluates the specific pore volume and PSD from the quantity of free and adsorbed gas.
(3) Low field Nuclear Magnetic Resonance (NMR) that qualifies and quantifies the magnetic response of proton under specific sequence(s) of applied magnetic fields that are dependent on the volume of fluids and on the pore body size distribution.
(4) Image acquisition techniques such as scanning electron microscopy (SEM) and X-ray computed tomography to visualise the core material.

In addition, most research methodologies are based on one type of experiment or a combination of two to understand porous media. For example: X-ray computed tomography scanning to study gas storage and transport in Devonian shales (Lu et al., 1992); NMR to model transport mechanism (Kanj et al., 2009; Osment et al., 1990); Nuclear Magnetic Resonance (NMR) and micro-CT scanning as a validation for pore network models (Talabi et al., 2009); NMR and X-ray small angling scattering to characterise pore system and flow characteristics (Bustin et al., 2008); a combination of scanning electron microscopy (SEM) and thin section analyses to determine mineral content, distribution and pore structure of Baker dolomite, Bera sandstone and Indiana limestone samples (Churcher et al., 1991); mercury injection (MICP) and scanning electron microscopy for petro-physical characterization of shale (Kale et al., 2010a,b); and focused ion beam (FIB) and MICP to compare pore bodies of mudstones (Heath et al., 2011).

To date there is no certain method for shale gas assessment, and many labs do not provide the approach, perhaps for competitive reasons (Bustin et al., 2008). This work compares the results from MICP with NMR and N2 to understand the pore network characteristics of organic-rich shale gas samples from Permo-Triassic Kockatea and Carynginia formations from the Northern Perth Basin. To our knowledge there is no published pore size assessment on the two shale formations in the literature. FIB/SEM image analysis was used to further verify the pore size at sub-micron scale and help to support laboratory pore structure analysis interpretations. FIB/SEM is a new and promising technique able to see pore details at the nanometer scale; it is not yet widely used in research because of technical challenges and time consuming image processing. The advantages and the shortcomings of the methods for PSD of shale samples are discussed as well.

2. Methodology

2.1. Sample collection

A total of eight shale samples are characterized in terms of their pore size structures. They all come from the most prospective part of the Northern Perth Basin (Fig. 1), over the Dandaragan trough,