

Comparison of void volume for volumetric adsorption studies on shales from India



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ABSTRACT

Correct determination of void volume is essential for carrying out adsorption isotherm experiments accurately. This paper presents the void volume data of two as-received shales, namely Salanpur and KG shales, India. Void volume experiments are conducted using helium and argon at 40 °C and up to a pressure of ~9.2 MPa. Difference in void volumes measured using helium and argon are lying in the range of 0.4–1.2 % and 0.2–1.6 % for KG and Salanpur shale respectively. The standard deviation percentage of argon is twice of helium, suggesting void volume estimation using helium to be more accurate than argon.

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1. Introduction

Determination of methane adsorption capacity in porous shale is important for estimating the potential of a shale gas reservoir. Since a significant fraction of the gas in shale reservoirs is stored by adsorption mechanism, understanding of adsorption behavior of shale is important (Chareonsuppanimit et al., 2012). Shales are important unconventional gas reservoirs, in which 40–60 % of the gas is stored in adsorbed state (Lewis and Hughes, 2008). For estimating methane adsorption capacity of shale, adsorption isotherm (AI) experiments are carried out. The AI experiments using volumetric method are carried out in two stages: void volume determination and actual adsorption measurement. Void volume implies the amount of dead space that is present in the sample cell (SC) in an adsorption isotherm (AI) setup. Ross and Bustin explain void volume of SC to be the dead volume that comprises of free space in the sample cell and pore spaces within the sample that is not occupied by adsorbate (Ross and Bustin, 2007). Determination of void volume is the most critical step in an adsorption isotherm experiment since the amount of adsorbed gas is calculated using the previously calculated void volume data. Void volume is usually determined by volumetric method using an inert probing gas like helium, argon, etc. A known volume (mole) of

inert gas is allowed to fill in the SC containing the crushed sample. Since the inert gas does not get adsorbed onto the coal or shale samples, it results in increase in the free gas pressure of the dead volume. Measuring the change in pressure, the unknown void volume is calculated using the Real Gas Law. This procedure is repeated many times and in successive steps the gas is filled with higher pressure. The void volume is calculated for each step and then averaged. The average void volume value is used for subsequent adsorption calculation.

Two major sources of error involved in void volume determination as suggested by Ross and Bustin are: 1) averaging the void volume values for multiple pressure steps; and 2) selection of an appropriate inert gas (Ross and Bustin, 2007). The averaging of all the void volume values obtained from different pressure steps may incorporate some errors in the adsorption calculation depending on the deviation of the exact void volume value at different pressure steps from the average void volume value. This error may lead to over/under-estimation of methane adsorption data depending on the positive or negative deviation (Ross and Bustin, 2007). The second source of error is related to the size of the inert gas molecule. Generally, helium is used as the inert gas for void volume determination. Helium has a smaller kinetic diameter (0.265 nm) compared to methane (0.380 nm). It is suggested that because of its smaller size, the helium molecule can enter very small pores which are not accessible to methane (Ross and Bustin, 2007). This results in a scenario where the entire void volume as determined by helium is not used for adsorption of methane. This phenomenon is

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known as 'molecular sieving' and is responsible for over-estimation of the void volume and underestimation of methane adsorption data (Ross, 2004). The negative adsorption data as seen in the studies of Bustin and Ross have been attributed to the error in the void volume calculation because of 'molecular sieving' (Ross and Bustin, 2007; Ross, 2004). Further, some studies have suggested that helium is not completely inert and although very negligible, it adsorbs on solid adsorbents at low temperatures and high pressures (Starzewski and Grillet, 1989; Malbrunot et al., 1997). As a result of the above two reasons, use of helium may result in erroneous calculation of void volume and subsequent erroneous adsorption data. It has been suggested that the error due to the molecular sieve effect can be eliminated by using other inert gas such as argon to determine the void volume (Ross and Bustin, 2007; Vermlyen, 2011). With a molecular diameter of 0.34 nm, argon is comparable to methane and it is suggested that error due to molecular sieving will be reduced.

As discussed above, the accuracy of the methane adsorption data is affected by the combined effect of the above two sources of error in calculation of void volume. The present study is intended to investigate the effect of change in the probing inert gas on the void volume value. The first objective of the investigation is to quantify the error in the void volume due to the averaging of the void volume data. The second objective is to study the variations in void volume of Indian shale samples, when two different inert probing gases, i.e., helium and argon are used, and to recommend the more suitable inert gas for void volume determination.

2. Experimental

2.1. Sample preparation

Two samples namely Salanpur and KG shales are used in the study. The Salanpur and KG shale samples are collected from Gondwana and Krishna–Godavari basins, India respectively. The as-received samples are crushed in the size range of 150–425 micron and 25–30 g of samples is taken for void volume experiment.

2.2. Void volume determination

The void volume experiments are conducted on a high-pressure setup using helium and argon, up to a pressure of 9.2 MPa and at a temperature of 40 °C as shown in Fig. 1. The experimental setup is based on the volumetric method of gas expansion technique (Boyle's law). The experimental set-up consists of fixed volume

stainless steel sample cell (SC) and reference cell (RC) separated by a two way ball valve. The RC is connected to a high precision pressure transducer (Makers – Druck & Leicester, UK; Maximum pressure – 25 MPa, Sensitivity – 2.5%; 0.05% of full scale). The entire set-up is placed in a constant temperature water bath with an accuracy of ± 0.1 °C.

2.3. Setup calibration (blank test)

Blank tests (sample cell without sample) are performed to ascertain the precision of volume measurements by the experimental setup. Blank tests were carried out using both helium and argon. The error in terms of standard deviation of blank test for helium and argon are calculated to be 0.12% and 0.11% respectively. This suggests that volume determination by the setup is precise and independent of the gas type.

2.4. Experimental procedure

The powdered sample is filled in SC and the SC is closed by tightening the nuts. The Swagelok SNOOP (Liquid Leak Detector) is applied on the fittings to detect any leakage in the setup. The RC is charged with the probing inert gas keeping the valve 1 (between the RC and SC) closed. In the first step, inert gas is filled in the RC to a pressure of approximately 1 MPa and the pressure readings are noted at intervals of 30 min until equilibrium pressure is achieved. If the consecutive readings are same then it is taken to be the equilibrium pressure. After the RC attains equilibrium, the valve 1 is opened. The pressure of the RC and SC is allowed to stabilize and the stable pressure is recorded. For the second step, valve 1 is closed and the RC is again charged with inert gas to a higher pressure (approximately 1 MPa higher than the previous value). This procedure is repeated for a number of times. For each step, the void volume is calculated using the real gas law. The void volume can be determined using the formula given below:

$$V_v = \frac{dnRTZ}{dP} \quad (1)$$

where V_v is the void volume, dn is the difference in number of moles in the RC and SC, R is the universal gas constant, T is the experimental temperature, Z is the compressibility factor of the probing gas and dP is the difference of two pressure steps in SC. The helium compressibility factor is calculated from the equation of National Bureau of Standards Technical Note 631 (McCarty, 1972). For argon, compressibility factor is calculated from the NIST software which uses Peng–Robinson equation of state (Friend, 1992). The void volume obtained in the multiple steps is averaged and the average void volume value is subsequently used for methane adsorption calculation purpose.

3. Results and discussion

The compositional analyses of the shale samples are performed. The TOC content of the KG and Salanpur shales are calculated to be 1.5% and 15.3% respectively. For KG and Salanpur samples, the clay minerals are estimated to be 41.8% and 12.5% respectively. It is clear that there is considerable difference in the TOC and clay mineral content between the two samples.

The experimental void volume data using helium and argon for KG and Salanpur shale are shown in Table 1. For KG sample, the void volume experiments using both helium and argon are conducted up to a pressure of 9.2 MPa in nine steps. The average helium- and argon-void volumes are calculated to be 150.2 ml and 150.6 ml respectively. For Salanpur shale sample, the void volume

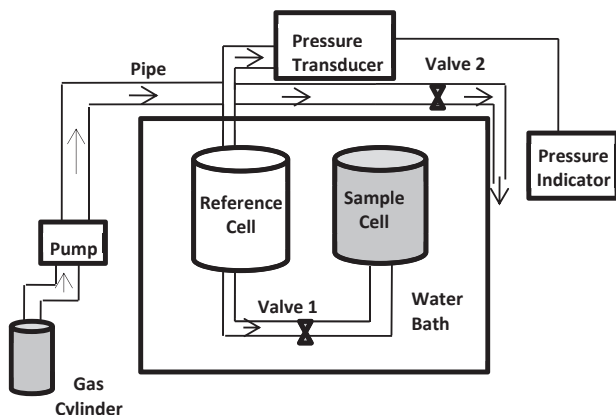


Fig. 1. Schematic diagram of adsorption isotherm setup.

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