On Void Volume Determination in Clay Rich Shale

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Abstract- Unconventional reservoirs such as shale have become an important and available possibility to meet the increasing demand on energy worldwide. Gas reservoirs like shale have a large untapped reserve of gas in adsorbed form in both the organic and clay rich component of the source rock. The secret to unlocking these reserves lies in accurate experimental data which in turn depends on the experimental method used. Recently a number of procedures such as manometric, volumetric and gravimetric have been developed to quantify adsorption, which requires the determination of "void volume" using helium. In the context of this research on understanding the source of inaccuracies in adsorption data from void volume of Clay- rich shale, an experimental method was used which does not quantify void volume directly. The advantage of this method is that errors due to primary measurement of parameters are reduced. A series of low pressure void volume measurement were performed on dry and water saturated sand stone sample representative of an ideal shale inorganic component at 230C and Helium pressures of up to 95Psia under dry and water saturated conditions. Experimental results indicate that there was a small variation in average void volume with pressure for the Bandera Gray and Scioto samples. The pressure ranges investigated showed close results regarding the measured void volume value with measurement scattered about an average of 8.017cm³ for Bandera Gray, and 4.5171cm³ for the Scioto samples. Water content in clay rich shale impacts void volume because water blocks some of the pores accessible to helium and leads to a decrease in void volume, therefore when quantifying storage in clay rich shale which is water wet, correction must be made to account for water in its various form (free, adsorbed and gas solubility in water) or errors might arise. The investigation indicates that water content of 5.62 wt. % and 5.48wt. % for both samples respectively, can reduce the dry capacity by as much as 12.53% and 11.2%.

Keywords - Void Volume, Clay rich Shale, Shale Adsorption

I. INTRODUCTION

Unconventional source of energy such as shale will be the future of natural gas exploration if accurate and innovative methods are continuous developed as highlighted by ongoing trends in the natural resources sector. For this to be achieved ground breaking research have to be carried out in the laboratory, the reason for this is that both free and adsorbed gas have been discovered in shale. For the later to be released important experimental procedures such as void volume determination must be taken seriously as it impacts the richness of adsorption data. These measurements are carried out using gas expansion methods based on Boyle's law with helium as a non-adsorbing gas; this technique is considered among the most accurate for measuring void volume as part of adsorbed gas component (or excess adsorption) quantification. Helium is used because it has been shown to give accurate quantification of void space, hence sample volume (Ross & Bustin, 2007; Heller and Zoback,2015). It has a great deal of properties which make it a perfect choice for void volume determination. These properties include; lack of its chemical reactivity (inert), does not have sorption capabilities at room temperature (Lu et al., 1993, 1995; Krooss et al., 2002; Goodman et al., 2004, Zhang et al, 2011), and does not adsorb on rock & clay surfaces (Anovitz and Cole, 2015).Because of the importance of void volume measurement in relation to adsorption data, researchers have made ground breaking contribution to literature through experiments with the aim of understanding the source of inaccuracies in adsorption measurement recurring from void volume measurement. (Ji, Zhang, Milliken, Qu, & Zhang, 2012) carried out helium expansion experiment at five pressure points (0.65 -15 MPa) and three temperature range ($35^{\circ}C$, $50^{\circ}C$ and $65^{\circ}c$). Helium void volume experiment was performed at each temperature individually, concluding that this was the most efficient way of correcting error by caused by temperature change in void volume calculations. In a later study (Zhang, Ellis, Ruppel, Milliken, & Yang, 2012), the authors based their study on a reasonable assumption that the void volume will remain constant over the temperature range of 35°C to 65°.

Ross and Bustin, (2007) investigated the effects of pressure, time and pore size distribution on the Helium void volume. They concluded that experimental analysis reveals that an overestimation of void volume by Helium which had an impact on the form of negative adsorption values. They identified contributing factors as Helium molecules have a smaller kinematic diameter than other gases and can penetrate in holes that others cannot, void volume changes by time, pressure, and temperature. There has been reports that errors in experimental data when quantifying excess sorption isotherms have been contributed by void volume inaccuracies (Gasparik et al, 2014). In a number of journal, studies conducted with the aim of quantifying the impact of pressure on void volume have proved that pressure does not influence void volume. Experimental investigation conducted conclude, not observing any noticeable difference with pressure in void volume measurements (Gasparik et al, 2012, 2014, Chareonsuppanimit et al, 2012, Heller and Zoback, 2014); wherein the authors conducted measurements using different pressure ranges, mostly at high pressure. There have been exceptions however where pressure has been shown to impact void volume (Ross and Bustin, 2007) using shale, clays and quartz samples. Chareonsuppanimit et al, (2012) observed that the void volume calculated from sequential injections varied less than 0.3 cm³ from an average reading of 60 cm³ from their experimental result. This view was also upheld by Heller and Zoback, (2014) who reported void volume data gravitating about a mean of 14.956ml with a deviation of 0.0045ml. Heller and zoback (2014) measured the reference cell volume over a range of equilibrium pressures. However, they observed no variation in void volume with pressure.

Water is paramount in shale reservoirs because it is found in different forms (free, adsorbed and soluble in gases), also used in hydraulic fracturing as fracturing fluid when drilling shale gas reservoirs. In the science of characterising shales, water saturation quantification can be demanding and full of inaccuracies (Agorudande et al, 2012). Data from studies relating to water saturation show large variation in results, this can be attributed to a lacking in method which could be used as standard reference standard (Clarkson et al, 2011, Sondergeld et al, 2010) with the implication being poor reproducibility of results between interlaboratory studies. A number of factors make water saturation in shale important include: The ability of water to block potential sorption sites (Rexter et al, 2014), water at different electrolyte concentrations which is used as fracturing fluid may cause volume changes of clay particles leading to corresponding changes in conductivity (e.g. Mitchell, 1976), also in systems such as shale which has a number of multiple phase system with numerous processes such as gas diffusion which is a continuous process may occur through the water saturated pore space, within the matrix or micro pore system of dispersed organic matter and along mineral surfaces (Hildebrand et al, 2011). Furthermore, moisture affects methane sorption in both organic and clay rich shales by about 40-90% (Rose, 2007, Gasparik et al,2014. Problems tend to arise because studies in water saturation in shales done in the laboratory are done according to such standard like the ASTM standard while the dynamics of water saturation in shale is under actual conditions(Li et al,2015).Clay minerals of shale are hydrophilic, making inorganic pores surrounded by water molecules or movable water, which dissolved only a few amounts of gas molecules. Water is trapped in inorganic pores, cannot be fully transpirated during hydrocarbon generation and gas output stage of kerogen. The clay contents of shales are about 30-50 %(Zhao et al, 2015). The impact of water and moisture in coal reservoirs using laboratory methods is well documented (Ekerem and Schroeder, 2009; Billemont et al., 2013; Svabova et al., 2011, 1974; Krooss et al., 2002; Gensterblum et al., 2013; Clarkson and Bustin, 1999), whereas studies related to shale (Gasparik et al., 2013, 2014; Ross and Bustin, 2007; Tan et al., 2014; Yuan et al., 2014, Merkel et al, 2015) are few.

This work was motivated by the research gap in understanding the impact of experimental parameters (pressure, time and water) on void volume of clay rich shale and its impacts on methane adsorption. which we hope will lead to more accurate adsorption data and a new understanding of the dynamics of void volume calibration in inorganic rich shale.

II. METHODOLOGY

A. Grain volume determination -

Helium pycnometry measures grain volume (often called skeletal density, apparent density, true density or absolute density), which is the density of a substance excluding pores large enough for helium to penetrate (Webb and Orr, 1997). A PORG-200[™] Porosimeter (Fig.1.2), a manually-operated helium pycnometer incorporating digital technology (11 Princess Road, Suite H Lawrenceville, NJ 08648, and U.S.A) was used to determine the void volume in samples studied. This instrument operates by detecting the pressure change resulting from gas displacement by a solid sample with helium as a non-adsorbing gas; this technique is considered among the most accurate for measuring grain and in turn the void volume as part of adsorbed gas component (or excess adsorption) quantification. Helium is used because of its various advantages (McCarthy and Arp, 1990; Arri et al., 1992; Mohammad et al., 2009a; Chareonsuppanimit et al., 2012).



Figure 1. Design layout of Core lab porg200 helium pycnometer

The helium pycnometry operational procedures used to determine void volume is schematically illustrated in Figure 1:



Figure 2. Schematic representation of manually-operated gas pycnometer

Before any tests, pressure testing was done to ensure that the system is leak tight. The PORG-200[™] was powered up thirty minutes before samples were to be run in order to allow the transducer to reach equilibrium. During this time, the gas supply pressure was set at 120 psig for the helium supply. The matrix cup (or optional core holder) was then attached to the helium outlet on the front panel of the instrument. Valve 2 was then turned to the vent position and Valve V1 was opened. The regulator was set to approximately 95 psig and Valve 1 was then closed. Turning Valve 2 to expand, this leads to a pressure drop which stabilizes immediately. The pressure was observed for 10 to 20 minutes. If the pressure continues to drop, there is a leak in the system. The helium source was turned off and Valve V1 was opened, turning V2 to expand (to the open matrix cup). The pressure reading on the digital readout was showing zero.

The experimental procedure involves, placing the sample with a known bulk volume (V_b) into a sealed matrix cup (V_c) . Gas is charged into a reference cell (V_r) at a predetermined reference pressure (P_1) , which is higher than the pressure (P_2) into the matrix cup. The reference cell gas is then expanded into a connected chamber of known volume containing a core sample by opening a valve between the two cells. The pressure of the system is then allowed to equilibrate until a stable value is observed. The grain volume, which will be used to calculate the measured void volume can then be calculated as follows:

$$V_{g} = V_{c} - V_{r} \left(\frac{p_{1} - p_{2}}{p_{2} - p_{a}} \right) + V_{v} \left(\frac{p_{2}}{p_{2} - p_{a}} \right)$$
2

Where:

Vg	=	Grain Volume
Vc	=	Sample Chamber Volume
Vr	=	Reference Chamber Volume
Vv	=	Valve Displacement Volume
P_1	=	Absolute Initial Reference Volume Pressure
P_2	=	Absolute Expanded Pressure
Pa	=	Absolute Atmospheric Pressure Initially in Sample Chamber

B. Bulk volume -

Bulk volume is the total volume of the sample including particle volume, inter-particle void volume, and internal pore volume. Bulk volume can be calculated accurately from the dimensions of a core sample if it is a true right cylinder and there are no surface irregularities. Using a caliper to obtain several diameter measurements and several length measurements, the average diameter and average length were used to calculate the bulk volume of the sample using the callipering method:

$$V_b = \pi r^2 L$$

3

Where, r is the radius of the cylinder, L is the length and π is a mathematical constant, the ration of a circles circumference to its diameter, commonly approximated as 3.14159.

Table - 1 Bulk volume calculated using callipering method:

Reading	Scioto		Bulk Volume	Bandera Gray		Bulk Volume
	Radius(cm)	Length(cm)		Radius(cm)	Length(cm)	
Average	1.2590	7.6685	38.17 <i>cm</i> ³	1.2560	7.6650	38.22 <i>cm</i> ³

C. Pressure calibration -

To investigate the influence of different pressure range on void volume values, the sand stones as received weight (i.e. the sample weight and moisture content) in grams where determined using a KERN Precision balance 440(KERN & SOHN GmbH, Ziegelei 1, 72336 Balingen – Germany). Samples were then dried in an ofite instrument – 173-001-1-Re oven (7979 Willow Chase Blvd. Houston, TX 77070, US) for at least 48hrs at 60° c, this is because heating the samples at higher temperature might alter the clay properties (Aljaman et al,2015) with sample weight being monitored until a constant weight was achieved. Then using incremental reference pressures of 15 psi, 45psi, 65psi, 85psi and 95psi.An initial reference pressure of 15psi was expanded into a volume containing the sample, after allowing 30 minutes for the system to reach equilibrium. The expanded pressure in the sample volume was then recorded; the same step was repeated until all pressure steps were carried out. The temperature of the system was also recorded for each experiment conducted.

D. Void Volume, Grain volume and Porosity -

The definition of void volume (V_v) in this study refers to the free space within the matrix cup and Pore volume within the sample excluding the surface available for gas adsorption. The pore volume is the void space in the rock while bulk volume (V_b) is the volume that the rock occupies, sometimes called matrix volume. Thus, void volume was calculated from the bulk volume and grain volume measurements:

$$V_v = V_b - V_g$$
 4

Where, V_v , V_b and V_g are the Void volume, Bulk volume and Grain volume respectively. Grain volume is the volume of the rock grains or solids (not including the pore volume). Porosity is the fraction of void space in the total rock.

E. Equilibrium time -

Test to examine the influence of equilibrium time on void volume values involved weighing the samples, and drying the samples in an ofite instrument – 173-001-1-Re oven (7979 Willow Chase Blvd. Houston, TX 77070, US. The temperature was kept at 60° c for 48hrs. Once a constant weight was achieved; the samples were then placed into the matrix holder of the helium pycnometer. Helium expansions were carried out on the sample, once an equilibrium time of 30mins was reached, expanded pressure values was recorded at 4 minutes internal for about (240mins)4 hours at a constant temperature of 23° c.

F. Water content determination -

In this work, the amount of water content was determined by drying the sand stone samples at 100° C over a period of 48hrs in an ofite instrument – 173-001-1-Re oven (7979 Willow Chase Blvd. Houston, TX 77070, US) and then saturating the sample in water for 48 hrs. For each determination, the water content, was calculated from the mass loss using Equation 4:

$$w_c = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100$$

Where, m_{drv} is the mass of the dry sample, m_{wet} is the mass of wet sample.

III. RESULT AND DISCUSSION

Helium (He) pycnometry as a method of determining grain volume and in turn void volume of porous solids such as inorganic shale has the "advantage of giving a sample volume (and therefore a location of the dividing surface) which is, by definition, perfectly reproducible from one adsorption bulb to another and from one laboratory to another" (Roquerol et al, 2009). In order to investigate the influence of a range of process variables on void volume measurements), rigorous experimental work was conducted. The investigation examined:

- 1. Pressure differential (the pressure at which the void volume was determined).
- 2. Equilibrium time, the equilibrium time at which the experimental reading was taken
- 3. Water content, which can be the formation water or water used in hydraulic fracturing during production which is commonly found in rich clay shale.

This section presents and discusses the data from the experimental work.

A. Effect of pressure on void volume -

Experimental uncertainties recurring from the use of helium as the gas of choice for void volume determination are associated with pressure and equilibrium cell volume (Mohammed et al, 2009, Gasparik et al, 2014). In order to investigate the influence of pressure on void volume determination using helium expanded on core samples representative of clay-rich shale, a series of investigations were undertaken in the laboratory at low pressure ranges. Helium expansions were carried out at pressure ranges of 15 to 95 Psia until pressure equilibrium was achieved for both samples.

Figure 3 reports the calculated void volume as a function of different pressure for the two clay-rich samples studied. Figure 3(a) shows the effects of different pressure on measured void volume for Bandera sample, while Figure 3(b) shows the result for Scioto sample. Figure 3(c) and 3(d) shows the standard deviation of data of Scioto and Bandera samples respectively, while Figure 3(e) and Figure 3(f) shows the percentage error of data.





Figure 3. The influence of pressure, the error bars represent the standard deviation of five pressure measurements.

Table 2 and Table 3 show the experimental result for measured void volume at low pressure ranges (15 - 95Psia) for the two samples studied:

Bulk Volume	Reference Pressure (psia)	Void Volume $(V_v)(Cm^3)$
	15	8.0169
38.22 cm ³	45	8.0167
-	65	8.0171
-	85	8.0171
-	95	8.0172

Table - 2 Helium void	volume at	different	studied	pressures	for Bandera	Gray
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15	4.5179
45	4.5169
65	4.5170
85	4.5169
95	4.5168
-	45 65 85 95

Table - 3 Helium void volume at different studied pressures for Scioto

The result in Figure 3(a) and Figure 3(b) indicate that there is very small variation in void volume with pressure for the Bandera Gray and Scioto samples. The pressure ranges investigated for both core samples (Bandera gray, Scioto) show similar results regarding the measured void volume value.

Figure 4.1(c), and Figure 4.1(e) and indicate that void volume measurement scattered about an average of 8.017cm³ for Bandera Gray, while Figure 4.1(d) and Figure 4.1(f) shows average standard deviation value of 4.5171cm³ for the Scioto samples. This shows that for both samples (Bandera and Scioto) studied, the experimentally determined void volume were close for each pressure range. This result agrees with published findings (Heller & Zoback, 2014) for Eagle Ford shale samples; they also found that pressure does not influence void volume value. Two separate studies carried out by Gasparik et al, 2012, 2014) using pressure range of up to 15MPa led to the same concluded that helium expansion data did not show any change with pressure.

Pressure is an important variable in excess methane gas adsorption in clay rich shale, which increases with respect to storage volume and can lead to a decrease in volume available for free gas or the void volume (Mohammed et al, 2009). Experimental data from this work, however indicate a constancy of average void volume change with pressure indicating that there was small increase of helium density at the surface of the investigated samples (adsorption) in observable quantity such as it has no influence in the void volume for both samples investigated. If helium was adsorbed at those rates, then the pressure would have increased at an exponential rate thereby resembling an adsorption isotherm (Ross and Bustin, 2009; Chareonsuppanimit et al, 2012). Furthermore, the experimental values indicate that at low pressure ranges, the amount of gas unabsorbed completely approaches the helium void volume e.g. $V_{p} = V_{ads}$ at low pressure ranges (Mohammed et al, 2009).

Another noticeable feature in Figure 4.1 9(a) and (b) is the scattering of measured void volume data about a mean, this seem to be an issue of methodology (Gasparik et al, 2014). The reason for this difference is that void volume calculation are carried out using different approaches such as pressure ratio (Bustin et al, 2009), differential and cumulative (Gasparik et al, 2014), equation of state (Heller and Zoback, 2014) and in this study, using grain volume calculation. These methods are all reliable and precision guaranteed, the only difference is that some might reduce the noise associate with large data as proved by Gasparik et al, (2014). It is largely a matter of preference and experimental set-up.

B. Effect of water on void volume measurement

Water saturated Bandera and Scioto samples were used in this research to investigate the effect of water on the calculated void volume. Table 4 presents the calculated water content of each sample, and Table 5 informs about the measured void volume in response to water. Figure 4 presents measured water saturated void volume as a function of pressure for samples analysed.

Table- 4 Water content of samples	
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Core Sample	Wet Mass (g)	Dry Mass(g)	Water content (%)
Bandera Gray	89.41	84.65	5.62%
Scioto	88.17	83.59	5.48%

Table - 5 Measured water saturated void volume for Bandera Gray and Scioto

	Void Volur	ne(cm ³)
Pressure(Psia)	Bandera Gray	Scioto
15	7.011	4.008
45	7.0121	4.0126
65	7.0140	4.0120
85	7.0132	4.0117
95	7.0131	4.0115

Table - 6 Comparison of measured Dry and Wet sample void volume

Pressure	Bandera Gray		Scioto	
_		Void Vo	lume (cm ³)	
_	Dry sample	Wet Sample	Dry Sample	Wet Sample
15	8.0169	7.011	4.5179	4.008
45	8.0167	7.0121	4.5169	4.0126
65	8.0171	7.0140	4.5170	4.0120
85	8.0171	7.0132	4.5169	4.0117
95	8.0172	7.0131	4.5168	4.0115



Figure 4. Impact of pressure on measured void volume of water saturated samples

Figure 4(a) and Figure 4(b) indicates that water does not have an impact on pressure with respect to calculated void volume for wet samples. The void volume value scattered about a mean of 7.0127cm³ and 4.0011cm³ for Bandera and Scioto sample respectively.

Table 6 presents a comparison of dry and water saturated measured void volume for Bandera Gray and Scioto sample respectively. Data indicate that water content of 5.62 wt. % and 5.48wt. % for Bandera and Scioto respectively can reduce the dry sample void volume by as much as 12.53% and 11.20% for investigated Bandera and Scioto samples. The experimental data above indicates that water blocks some of the volume accessible to helium and this in turn is propagated as a decrease in void volume available for helium. This has been observed

(Ross and Bustin, 2007), who conclude that water both in adsorbed and free form blocks the pore space available to helium. Furthermore, void volume is usually determined on dry basis and applied to methane adsorption isotherms of wet clay rich shale samples. Even though each shale has individual unique properties, with some shale having zero to non-water initial content as indicated by researchers (Makhanov et al., 2014; Wang et al., 2009). Majority of shale especially clay rich shale is water saturated (Jarvie, 2012). However, Mohammed et al, (2009) reports that with respect to helium void volume determination, a number of assumption are taken such as; water exist in free state, in adsorbed form and the solubility of gas in water. The preceding statement overall indicates the complexity of water content in void volume determination, as it adds complexity to the number of variables which needs to be solved for accurate measurements. In this investigation, we propose that corrections must be made when quantify void volume for clay rich shale which is water saturated. It has been shown however that for helium void volume determination for coals no water-rich phase is assumed to exist. The water in a system container is adsorbed completely (Mohammed et al, 2009). This modification involves accounting for the different variable (Moghaddam, 2013, Khosrokhavar et al, 2012):

Where, N is the number of experimental steps, ΔV_{ads} is the volume of water adsorbed on the surface of shale, ΔV_{sw} is the effect of swelling and the reaction of adsorbed gas with shale(ΔV_{rec}).

C. Effect of equilibrium time on void volume calculation

Equilibrium time is a critical factor in void volume determination because it affects the measured void volume value (Ross and Bustin, 2007). The aim of this analysis was to compare the impact of longer equilbrium time on the measured void volume of the two sample studied at different pressure ranges of 15 to 95Psia. Figure 5 shows the impact of equilibration time on the final calculated void volume value for Bandera samples. Figure 5(a), 5(b), Figure 5(c), Figure 5(d) and Figure 5(e) show the influence of equilibrium time after 240 minutes for 15, 45, 65,85 and 95 Psia respectively. Figure 6 presents a comparison of equilibrium time for different pressure range investigated.

Figure 7 shows the impact of equilibration time on the final calculated void volume value for Scioto samples. Figure 7(a), 7(b), Figure 7(c), Figure 7(d) and Figure 7(e) show the influence of equilibrium time after 240 minutes for 15, 45, 65 and 95 Psia respectively. For comparison purposes, measured void volume as a function of equilibrium time are presented in Figure 8 for pressure ranges investigated for the Scioto sample.





Figure 5. Impact of equilbrium Time at investigated pressure ranges for Bandera Gray

Several minutes are allowed for thermal equilibration, and pressure readings are taken every 4 min for 240 minutes (4 hour) period, thus the void volume could be measured with respect to time. Figure 5(a-e) illustrates that the calculated void volume overall increases with time for the pressure ranges (15 - 95Psia) investigated until it attaines a saturation point and then increases linearly. The increase of measured void volume with time is the result of diffusion of helium into the sample, which increases with time and leading to access of finer pores within the investigated samples (Ross and Bustin, 2009).



Figure 6. Comparison of equilbrium time at studied pressure ranges on void volume for Bandera

Figure 5(a-e) shows that as equilibrium time increased, leading to more access of minute sizes of pores, accurate void volume is suggested from measured void volume for different equilibrium times (i.e. the time interval between the equilibrium of the cell and recording of matric holder pressure) at studied pressure ranges (15 - 95Psia) for the Scioto sample.





Figure 7. Impact of equilbrium Time at investigated pressure ranges for Bandera Gray

For the effect of time on measured void volume for Scioto sample (Figure 8), it can be seen that after 200 minutes, the measured void volume becomes stable at the five pressure ranges. This indicates that Helium gas has filled all accessible pores and has reached equilibrium.



Figure 8. Comparison of equilbrium time at studied pressure ranges on void volume for Scioto

The experiments indicate that ensuring sufficient time to reach equilibrium is critical for the accuracy and precision of data. The same observation was noticed by Ross and Bustin, (2007) as well; they concluded that the increasing trend in void volume with time is as a consequence of the ability of helium to diffuse into smaller void spaces with time. In another study Gasparik et al, (2013) they suggested that due to very low permeability of shale, the equilibration times for core samples can be as high as > 10 h. Hence, the results from rapid measurements often encountered with commercial pycnometers can be in large error. Therefore, in order to measure accurate void volume, it is necessary to wait for a long period of time until the gas pressure reaches an equilibrium saturation point.

IV. CONCLUSIONS

Using Helium Pycnometry apparatus as a measurement tool for void volume of sandstone samples (Bandera, Scioto) representative of clay rich shale, a number of parameters were investigated: Pressure, Equilibrium time,

water content, grain volume and porosity. Data was presented which documents the effect of pressure, time and water content and the effect of the inaccuracies in void volume data. Void volume data showed that there was no small variation in void volume with pressure for the Bandera Gray and Scioto samples. The pressure ranges investigated showed close results regarding the measured void volume value with measurement scattered about an average of 8.017cm³ for Bandera Gray, and 4.5171cm³ for the Scioto samples.

Equilibrium was attained after a 240mintes (four hour) interval. Investigation revealed that longer times yielded better void volume data, this is because as equilibrium time increased, helium was able to access of minute sizes of pores as a result of its small molecular diameter. Water content in clay rich shale impacts void volume because water blocks some of the pores accessible to helium and leads to a decrease in void volume, therefore when quantifying storage in clay rich shale which is water wet, correction must be made to account for water in its various form (free, adsorbed and gas solubility in water) or errors might arise. The investigation indicates that water content of 5.62 wt. % and 5.48wt. % for both samples respectively, can reduce the dry capacity by as much as 12.53% and 11.2%.

NOMENCLATURE

Psi pound per square inch = ^{0}C = Degree Celsius Cm = Centimetre In = Inch р = Pressure r = radius L = length π = pi V_{h} = Bulk Volume V, Void Volume = Vg Grain Volume = Vc = Sample Chamber Volume V_r = Reference Chamber Volume Vv = Valve Displacement Volume P_1 = Absolute Initial Reference Volume Pressure P_2 = Absolute Expanded Pressure Pa = Absolute Atmospheric Pressure Initially in Sample Chamber

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