WATER VAPOUR ADSORPTION ISOTHERMS AND MERCURY INTRUSION POROSYMETRY FOR DETERMINATION OF PORE CHARACTERISTICS OF SHALES

Chandrakant S. Gokhale

Professor, National Institute of Construction Management and Research, Pune, India-411045 (e-mail of corresponding author: cgokhale@nicmar.ac.in)

ABSTRACT

The Shales are extensively encountered during various mining, tunneling, civil engineering activities and oil and gas exploration activities. The shale is a potential source rock for gas and oil exploration as well as for geothermal energy. The pore size distribution in porous rocks like shales has a great bearing on the three important and inter-related hydraulic properties viz. porosity, permeability and fluid and gas storage as well as transport capacity. The knowledge of pore size distribution of rocks is very much essential to understand the problems related with underground openings, flow patterns through reservoir, drilling of oil and gas wells, stability of deep bore wells etc. It controls the storage mechanism and reservoir fluid properties of the permeable horizons. The paper presents and discusses the results of experimental investigation conducted to understand complete pore size distribution of shales obtained through Water Vapour Adsorption Isotherms (WVAI) method as well as Mercury Intrusion Technique (MIT).

Keyword: Mercury intrusion, Pore volume, Shale, Surface area, Water vapour adsorption isotherm,

1 Introduction

The sedimentary rocks are commonly encountered during various civil, mining and tunnelling engineering construction activities. In terms of area of exposure, the sedimentary rocks constitute about 75% of all rocks as reported by Pettijohn, 1984, [1]. Further the three principal sedimentary rocks viz. sandstone, limestone and shale account for above 80% of all sedimentary rocks. The Shales are extensively encountered during various mining, tunneling, civil engineering activities and oil and gas exploration activities. The shale is a potential source rock for gas and oil exploration as well as for geothermal energy.

The pore size distribution in porous rocks like shales has a great bearing on the three important and interrelated hydraulic properties viz. porosity, permeability and fluid and gas storage as well as transport capacity. It also plays a significant role in influencing physical, geophysical and geotechnical behaviour. The knowledge of pore size distribution of rocks is very much essential to understand the problems related with underground openings, flow patterns through reservoir, drilling of oil and gas wells, stability of deep bore wells etc. This emphasises the need to conduct studies on pore size distribution to understand various behavioural aspects of porous rocks. In the past, research workers attempted to understand the behaviour of porous rocks mostly on the basis of porosity and void ratio which gives an idea about total pore volume only. However, very little attention has been given towards the pore size and pore volume distribution in rocks. In view of the above, recently studies are being undertaken by researchers to understand behaviour of porous rocks through their detailed pore structure analysis. The study of pore characteristics is of great importance in shales. It controls the storage mechanism and reservoir fluid properties of the permeable horizons.

2 Estimation of Pore Size Distribution in Rocks

There are two commonly used methods to estimate pore size distribution of rocks in laboratory. These two methods are outlined in brief below.

2.1 Water vapour adsorption method

This method is based on Kelvin's capillary condensation equation (Equation. 1) and multi-layer adsorption theory of Brunauer et al., 1968, [2].

$$\log_{n}(p/p_{0}) = -2.\gamma' V'/RTr$$
⁽¹⁾

Wherein, p is the vapour pressure of a liquid adsorbate condensed in a capillary of radius r; p_o is the saturation vapour pressure of the adsorbate; γ' is surface tension of the adsorbate; V' is molar volume of the adsorbate; R is the gas constant and T is the temperature in Kelvin.

The method consists of obtaining water vapour adsorption isotherm (plot between relative pressure and equilibrium moisture content) experimentally. In order to obtain water vapour adsorption isotherm, dry rock specimens are exposed to different relative pressures i. e. relative humidity (R. H.) and equilibrated for long periods ranging from 1 to 3 months. For this purpose, generally aqueous solutions of acids are used in desiccators to maintain desired R.H. as reported by Lange, 1967, [3]. This method to obtain isotherm has also been referred by Anwar et al.; 1997, [4] as hygroscopicity test (The water vapour isotherms are then analysed to estimate pore radii, surface area and pore volume distributions.

2.2 Mercury intrusion technique

The mercury-penetration technique (usually called mercury intrusion porosimetry) is based on the fact that the mercury behaves like a non-wetting liquid when in contact with most of the solids. Consequently, it does not penetrate into the openings and cracks of these substances without application of pressure. The pressure (p) required is a function of contact angle (θ) of mercury with the porous material being intruded, its surface tension (γ ') and geometry of pores (pore radius r_p). This relationship expressed by Washburn equation (Equation 2) for special case of cylindrical pores.

$$P = -2\gamma'\cos\theta/r_{\rm p} \tag{2}$$

Schmidt et al., 1994, [5] determined pore size distribution for Tournemire shale, Vosges sandstone and Fontainebleau sandstone within a range of pore radii from 0.001 to 50 μ m. Their data indicate that for Tournemire shale (porosity 13.7%) more than 90% pore volume corresponds to pore radii in the range of 0.005 to 0.5 μ m with average value of about 0.1 μ m. The pore radii of Vosges sandstone and Fontainebleau sandstone (porosity 13.7 and 26.0% respectively) range from 0.1 to 20 μ m with average values of about 8 and 12 μ m respectively. Although Tournemire shale and Vosges sandstone exhibit exactly same porosity of 13.7% their average pore radii significantly differs, being 0.1 μ m and 8 μ m respectively.

Brignoli et al., 1995, [6] reported the pore size distribution for carboniferous sandstone, Bath limestone and Pietra Leccese chalk (having porosity 8.3, 23.1 and 34.0% respectively) for pore radii ranging from 0.0005 μ m to 100 μ m. The data indicate that over 90% of the pores of sandstone have average pore radius of less than 1 μ m whereas this value for limestone and chalk being about 2 μ m and 5 μ m respectively. The pore size distribution studies were conducted by Anwer et al., 1997, [4] on carbonate sandstone, volcanic sandstone and siltstone (the porosity for these rock ranges between 13% to 19%) for pore radius ranging from 0.0001 to over 10 μ m. Rao, 1984, [7] studied pore size distribution of 4 Indian sandstones and reported that by analysing the water vapour adsorption isotherms, pore radius in the range of 0.0025–0.2 μ m. could be conveniently determined. From the reported distribution it has been observed that the average pore radii for all these rocks ranges between 0.01 to 0.5 μ m.

In literature (Laskar et al., 1997) [8] for mercury intrusion method the volume of mercury retained in the specimen just after the de-pressurisation (V_{mr}) expressed as percentage of total volume of mercury intruded (V_{mi}) has been defined as retention factor, R_f . as given in Equation 3. Thus, R_f which is indicative of pores of small size and the pores with bottleneck, the quantity (100- R_f) will indicate the volume of large size pores.

$$R_{f} = (V_{mr}/V_{mi})x100$$
(3)

2.3 Complete Pore Size Distribution

The literature study on pore size distribution of rocks indicates that neither of method is suitable and capable to estimate complete pore size distribution. While the mercury intrusion technique is capable of estimating pore size distribution for a wide range of pore radius covering very fine pores to coarse pores. (Huang and Demirel, 1973 [9]. However, it requires application of very high pressure for measuring fine pores, e.g. as per Eq. (1), a pressure of about 75 MPa and 150 MPa is required to estimate pore radius of the order of 0.01 Am and 0.005 Am, respectively. The compressive strength of most of the medium to high strength rocks falls within this pressure range. Deere and Miller, 1966, [10]. The application of such a high pressure may lead to distortion in pore structure geometry as a result of breakage of cementing bonds and crushing of grains. This is the limitation of this method for its use to study pore size distribution of rocks with fine size pores. The water vapour adsorption method which is ideal for estimating fine pore sizes with fair degree of accuracy, may not estimate coarse pores correctly as a result of inadequate capillary condensation as reported by Gokhale, 1999 [11]. Therefore, the total pore volume and pore volume distribution estimated from water vapour adsorption method may have errors especially for coarse size pores. Water saturation method is also a direct method but it provides

only the total volume of pores. Thus, it appears from literature study that one has to use combination of data obtained from combination of methods so as to estimate complete pore size distribution. any single method in its present form is inadequate to obtain complete pore size distribution of rock.

3 Experimental Investigation

In order to understand the pore size characteristics of shales, the samples in the form of block samples were collected from two mining area location namely near Dudichua village in Sonebhadra district in Uttar Pradesh and from near Kotma village of Shahdol district in Madhya Pradesh and Uttar Pradesh and were subjected to elaborate experimental investigation. From the block samples specimens as required were obtained and subjected to various tests. The TABLE 1 presents the details of locations of these rocks. For brevity, they are referred as DSS (Dudichua-Sonebhadra Shale) and KSS (Kotma-Shahdol Shale)

Sr. No.	Location of	Procurement	Latitude	Longitude	Symbol
	Village	District			adopted
1	Dudichua	Sonebhadra	24.5N ⁰	$82.5E^0$	DSS
2	Kotma	Shahdol	$23.2N^{0}$	81.9E ⁰	KSS

Table 1 Location of Rock Samples

The physical properties of these two shales were obtained both at microscopic and macroscopic level. In order to evaluate the rock forming constituents, the experimental studies were conducted to understand its mineralogy and petrography through X- ray diffraction analysis, the studies of thin sections under microscope (magnification x20), scanning electron microscopy and chemical analysis was conducted following standard procedure. The macroscopic physical characteristics such as specific gravity, dry & saturated unit weights, effective & total porosities and water absorption have been determined in the laboratory following the ISRM suggested procedure edited by Brown, 1981, [12]. In addition, void index and water evaporation index were also estimated. In order to estimate pore size characteristics two methods were employed namely water vapour adsorption isotherm method (WVAI) and mercury intrusion technique (MIT).

3.1 Water Vapour Adsorption Isotherms

In this method, 3 specimens (l/d = 2.00) of each of two shales studied were equilibrated at 5 different relative humidities following the methodology reported by Gokhale and Deshmukh; 1994, [13]. Aqueous solutions of sulphuric acid (H_2So_4) were used to maintain the desired relative humidities in desiccators. Lange; 1967, [3]. The specimens were kept in air-tight desiccators at desired relative humidities (35%, 50%, 75%, 90% and 100%) at a constant temperature of $27\pm0.5^{\circ}C$ until equilibrium moistures were reached. The monitoring of specimen saturation was made by periodical weighing. Usually, a specimen was considered to have reached a given degree of saturation when periodical weighing showed constant weight at least for four consecutive days. The equilibrium moisture contents were determined in grams of water per gram of dry rock. Simultaneously, the density of H_2SO_4 solution in each desiccator was also determined to obtain the degree of relative humidity. The water vapour adsorption isotherms have been obtained by plotting equilibrium moisture content with relative humidity and are presented in Fig. 1.

Section A-Research paper



Fig. 1 Water vapour adsorption isotherms for Shales

3.2 Mercury Intrusion Technique

In order to obtain mercury intrusion curves, rock specimens of 25 mm diameter and length to diameter (l/d) ratio of 1.00 were prepared, which were dried first in an oven maintaining a temperature of 105° C to within 3° C for a period of at least 24 h and then cooled down to ambient temperature in a dry air tight desiccator. The tests were conducted in Autoscan-33 Mercury Porosimeter. Quanta Chrome; 1990, [14]. The mercury intrusion curve, i.e. volume of mercury intruded as a function of pressure was obtained through automatic x–y plotter. These tests have been conducted up to a maximum pressure of about 150 MPa, which corresponds to the intrusion of mercury into the pores of radius 0.005 Am or more. For each rock type at least three specimens have been tested and the mercury intrusion curves for shales thus obtained are presented in Fig. 2.



Fig. 2: Mercury intrusion curves for shales

4 Result and Discussion

The typical experimental data are presented and analyzed so as to assess the pore size characteristics and its classification.

Section A-Research paper

4.1 Mineralogy, Petrography and Chemical Composition

Geological DSS belongs to upper Proterozic age, Gondwana sequence stratigraphic belonging to Talchir formation. The other shale namely KSS belongs to upper Permian age, Gondwana sequence stratigraphic belonging to Damuda group. The mineralogical and petrographical studies have been carried out using petrographical microscopy of thin sections, x-ray diffraction and scanning electron microscopy. The dominant mineral present in each rock type is identified on the basis of these studies and its approximate percentage is also obtained through petrographical study and chemical analysis is also performed. On the basis of the study of x-ray diffractograms scanning electron micrographs (Figure 3) and petrographical analysis following observation are made.



(a) DSS

(b) KSS

Fig. 3: Scanning Electron Micrographs for Shales studied

Dudichua-Sonebharda Shale (DSS): This slaty-blackish coloured fine-grained rock has moderate to close packing of grains. It mainly contains clay minerals, quartz and organic matter. The alteration of mica and highly altered siliceous material has been noticed in this rock. This shale which shows traces of opaque minerals contain around 45% of quartz and 50% of clays.

Kotma-Shahdol Shale (KSS): This dark black coloured fine-grained shale contains clay, organic matter and quartz. The organic matter in this shale appears to be more than DSSH, whereas the quartz content is much less. It contains around 35% of quartz and 50% of clays. The presence of siliceous matrix and earthen opaque minerals have been noticed in this shale.

The summary of chemical composition of these two shales is presented in TABLE 2. It can be seen from the data given TABLE 2 that both DSS has higher percentage of SiO2 of about 65% while KSS has about 45%. Further the Loss on Initiation (LOI) for KSS is observed to be more than double (32.84%0 when compared to DSS (11.56%), with other chemical constituents being in close proximity.

Section A-Research paper

Rock	Chemical Constituents, %						Predominant Minerals		
Туре	SiO ₂	Al_2O_3	Fe ₂ O ₃	TiO ₂	CaO	MgO	LOI	Others	
DSS	65.10	18.29	2.27		0.84	0.60	11.56	1.34	Quartz, Kaolinite, Mica
KSS	45.20	17.29	2.13		0.84	0.40	32.84	1.28	Quartz, Kaolinite, Feldspar

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4.2 Physical Properties

The values of various physical properties viz. specific gravity (G), dry unit weight (γ_{dry}), saturated unit weight (γ_{sat}), total porosity (n_t), effective porosity (n_e) and water absorption (saturated moisture content, m_s) for the two shales studied are reported in TABLE 3. In addition, TABLE 3 also presents the magnitudes of effective degree of saturation, S_{re} [=(n_e/n_t). S_r], void index (I_v) and water evaporation index (I_{we}). Gokhale; 1999, [11] for the two shales studied. It can be observed from the data given in TABLE 3 while DSS has higher value of total porosity, KSS has higher values of effective porosity. Further DSS has higher value of effective degree of saturation, almost 20% more than that of KSS, clearly indicating that not the total pore volume but effective pore volume also plays a significant role in pore size and shape characteristics.

Rock	G	γ_{dry}	γ_{sat}	n _t	n _e	m _s	s _{re}	Iv	\mathbf{I}_{we}
Туре		KN/m ³	KN/m ³	%	%	%	%	%	%
DSS	2.66	20.59	22.17	16.23	21.11	7.71	77.04	5.01	2.78
KSS	2.56	19.16	20.53	13.95	23.69	7.15	59.12	4.78	2.12

Table 3 Physical Properties of Shales Studied

5 Pore Characteristics

The pore characteristics include various parameters such as total pore volume and surface area of pores and its distribution as a function of pore radius. The water vapour adsorption isotherms for shales illustrated in Fig. 1 show segmental increase in equilibrium moisture content (EMC) with increase in relative pressure (p/ps). The mercury intrusion curves obtained from the mercury intrusion porosimetry tests conducted on the specimens of sandstones and shales are presented in Fig. 2. In general, these curves show initial rapid increase in volume of mercury intruded (V_m) with increase in pressure (p) and beyond a value certain value of p they become asymptotic beyond a pressure of about 25 MPa. The water vapour adsorption isotherms obtained for shales and presented in Fig. 1 have been analysed using the method proposed by Brunauer et al.; 1967 [10] and following the methodology of calculation suggested by Gokhale and Deshmukh; 1994, [12]. The mercury intrusion curves obtained for shales and presented in Fig.2 have been analysed for their pore size distribution by adopting the method as per Quanta Chrome; 1990, [14]

5.1 Pore volume distribution

The variation of Pore volume (V_p) and pore radius (r_p) curves for both the shales obtained by analysing both water vapour adsorption isotherm as well as mercury intrusion curves are presented in Fig. 4. The curves obtained on the basis of analysis of WVAI show initial marginal increase, followed by very steep increases and as r_p becomes 0.01 µm they become asymptotic. In contrast the variation obtained by MIT continue to show moderate increase in surface area even and a value of r_p of about 0.001 µm. This clearly indicates that WVAI fails to estimate pore volume very fine pores having radius lesser that 0.01 µm. Thus, the comparison of curves in Fig. 4 clearly demonstrates that the pore volume distribution obtained by WVAI differs significantly from that by MIT for the shales studied.



Fig. 4: Pore volume distribution curves for shales

The volume of pores determined by WVAI and MIT expressed as a percentage of total pore volume determined from water saturation method for different pore radii ranges are presented in TABLE 4. The values of for r_p <0.005 µm is obtained as total pore volume by water saturation method less total pore volume up to 0.005 µm by WVAI/MIT.

Range of $r_p(mm)$	Percentage pore volume		Percentage pore volume		
	distribution for DSS		distribution for KSS		
	By WVAI By MIT		By WVAI	By MIT	
>0.80	00.00	00.00	00.00	00.00	
0.80-0.40	06.80	00.51	03.22	03.21	
0.40-0.20	05.64	00.78	02.03	00.98	
0.20-0.10	09.69	02.85	02.31	02.80	
0.10-0.05	11.62	17.90	05.65	21.27	
0.05-0.02	21.67	48.51	12.69	30.08	
0.02-0.01	11.58	00.00	11.68	03.36	
0.01-0.005	07.27	00.13	15.76	07.83	
< 0.005	25.73	29.32	46.66	30.47	

Table 4 Percentage Pore Volume Distribution of Shales Studied

According to pore volume classification reported by Gokhale; 1999, [10], the percentage of different size of pores for the shales studied is presented in TABLE 5. It can be clearly seen from data given in TABLE 5 that both shales have significant number of pores of very fine size and medium size. In fact, the total value of pores of these two sizes is about 84% for KSS and 95% for DSS.

Pore class	Range of pore radius $r_p(\mu m)$	V_{p} (%) for DSS	V_{p} (%) for KSS
Very Coarse	>0.50	0.38	3.41
Coarse	0.10-0.50	3.76	4.58
Medium	0.01-0.10	66.41	53.71
Fine	0.005-0.01	0.13	7.83
Very Fine	<0.005	29.32	30.47

Table 5 Pore Volume Classification of Shales Studied

It can be seen from the data and discussion presented that for the shales studied WVAI provides the reliable results of pore volume distribution for entire range of pore radius and there is no need to use the combination of methods to obtain complete pore size distribution. However, for some other rocks it may be advantageous of using low pressure data from MIT and remaining data from WVAI to obtain complete pore size distribution. Such a combination eliminates the application of high pressure in MIT which otherwise may cause compression of specimen, the breaking of cementing bonds, crushing of grains etc. and thereby altering the pore structure apart from the experimental problems associated with working in high pressure range.

5.2 Pore surface area distribution

The pore surface area (S_p) distribution curves for these shales obtained by WVAI and MIM as function of (r_p) presented in Fig 5. The curves obtained on the basis of analysis of WVAI show initial marginal increase, followed by very steep increases and as r_p becomes 0.01 µm they become asymptotic. In contrast the variation obtained by MIT continue to show moderate increase in surface area even and a value of r_p of about 0.001 µm. This clearly indicates that WVAI fails to estimate surface area or very fine pores having radius lesser that 0.01 µm.



Fig. 5: Pore surface area distribution curves for shales

6 Conclusions

This paper presents the results of experimental investigation conducted on two shales a potential source rock for gas and oil exploration as well as for geothermal energy to understand its pore structure characteristics which

plays an important role and controls the storage mechanism and reservoir fluid properties of the permeable horizons. The following major conclusions arrived at on the basis of above experimental results.

- Geological DSS belongs to upper Proterozic age, Gondwana sequence stratigraphic belonging to Talchir formation. The other shale namely KSS belongs to upper Permian age, Gondwana sequence stratigraphic belonging to Damuda group.
- (ii) Mineralogically both DSS has higher percentage of SiO2 of about 65% while KSS has about 45%.
- (iii) Chemically the Loss on Initiation (LOI) for KSS is observed to be more than double (32.84%) when compared to DSS (11.56%), with other chemical constituents being in close proximity.
- (iv) The experimental results indicate that while DSS has higher value of total porosity, KSS has higher values of effective porosity.
- (v) Further DSS has higher value of effective degree of saturation, almost 20% more than that of KSS, clearly indicating that not the total pore volume but effective pore volume also plays a significant role in pore size and shape characteristics.
- (vi) Both shales have significant number of pores of very fine size and medium size. In fact, the total value of pores of these two sizes is about 84% for KSS and 95% for DSS.
- (vii) The results of analysis of pore data clearly demonstrates that the pore volume distribution obtained by WVAI differs marginally from that by MIT for the shales studied.
- (viii) For the shales studied results indicate that WVAI provides the reliable results of pore volume distribution for entire range of pore radius and there is no need to use the combination of methods to obtain complete pore size distribution.
- (ix) WVAI estimates pore surface area distribution fairly, However, it has a limitation to estimate pore surface are very fine pores having radius lesser that 0.01 μm.

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