MORPHOLOGICAL STUDY OF SEAL ROCKS USING NITROGEN ADSORPTION ISOTHERMS AND MERCURY POROSIMETRY

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Abstract. The geometric and physical properties of the geologic materials, such as porosity and permeability, are important in various application fields and constitute technological and scientific interest. In the environmental field they are essencial among others in the remediations studies of contaminated areas, in projects of subterranean arrangement for nuclear trash. For the petroleum industry, those properties are of interest since they are directly connected to the productivity and efficiency of a reservoir. If earlier the attention used to be centered in reservoirs rocks, today better knowledge in seal rocks is desired. In the petrological geology seal rocks (also called cap rocks) are designed by rocks with a highly decreased permeability that can constitute barriers to the migration of the petroleum. The main parameters associated to the permeability are the specific surface area, the size, form, orientation and interconnection of the pores. It is knowledgeable that cap rocks present a heterogeneous pore microestructure.

In the present work, the pore size distribution, cumulative pore volume and the specific surface area of seal rocks were measured using the adsorption gas technique and mercury porosimetry. The analyzed samples were provided by the Cenpes/Petrobras. The BET theory (Braunauer, Emmet and Teller) was utilized for the determination of the specific surface area and the BJH model (Barret, Joyner and Hallenda) for the pore size distributions, both analyzed of the nitrogen gas adsorption. The results are presented, proceeding an analysis of the limitations involved in the used techique. Also, the datas of the pore size distributions and of the specific surface area were evaluated in empirical equations as a way to estimate the intrinsic permeability of the seal rocks. These values can be compared in the future using direct measurements of the permeability in some analysed samples.

Keywords: Seal rocks, N₂ adsorption, BET theory and BJH model, intrinsic permeability.

1. INTRODUCTION

Seal rock is a formation with extremely low porosity and permeability overlying an oil or gas reservoir, and it constitutes the barrier against the volume flow of hydrocarbons into the upper layers. Although a seal rock can be considered as a seal to hydrocarbons, it is erroneous to regard it as a completely impermeable layer (Li et al 2005).

The behaviors of breakthrough capillary pressure and permeability define the sealing efficiency of cap rocks. Many works have been published in the way of measuring the seal rocks properties and efficiency with experimental determinations (Okamoto et al, 2005; Schlömer et al, 1997; Hao et al, 2000; Bolas et al, 2005 e Hildenbrand et al, 2002). The sealing properties are considered beneficial in the context of petroleum and natural gas (CH₄) exploration and also increasingly important in the search for repositories to sequester waste (radioactive and nonradioactive) as well as in the storage of anthropogenic CO_2 in the subsurface, e.g. saline aquifers, exploited gas reservoirs (Hildenbrand et al, 2002).

The information regarding the porous system geometry and the physical properties in cap rocks are still relatively poor. If earlier the attentions were centered in reservoirs rocks, today the focus shifted to obtaining better knowledge in seal rocks. The wide mineralogical range of compositions adds a relevant problem in the quantitative evaluation and prediction of the stamping efficiency. Pape et al (1999), for example, reported that drastic permeability reductions result from the growth of minute amount of secondary clay minerals on quartz grains, since this changes the geometry of the hydraulic capillaries. They also relate it would be very difficult to explain the relationships between porosity (ϕ) and permeability (k) of different lithologies with a single empirical expression, however, most of them express k as the product of ϕ and a size parameter, taken to different material. This size parameter may be grain diameter, pore radius, or the specific surface.

In recent works the permeability of seal lithologies were found to range from 16 down to 0.1 nDarcy (nDarcy = nanodarcy; 1 nDarcy = 10^{-9} Darcy = 10^{-21} m²) (Schlömer et al, 1997). Yang and Aplin (2007) measured for 30 natural mudstones the vertical permeability ranging from 160 to 0.24 nDarcy.

Usually the microstructure of cap rocks is highly complex, very anisotropic and contains very small pore diameters (in Angstroms order). Therefore cap rocks morphology is difficult to characterize, making it necessary to use different methods that are complementary. Thereby it is usual to connect Mercury Intrusion and Gas Adsorption analyses. The first one is usable for the investigation in mesoporous whereas the second one is more fitted for the microporous analyses. Moreover, Hg porosimetry uses high pressures which may have some interference with the microstructure of the measured material.

We aimed to determine the distribution of the pore sizes in cap rocks by combining N_2 adsorption and mercury porosimetry to estimate the intrinsic permeability. For that an investigation of the pore size distribution range 20Å to 600Å with N2 adsorption isotherms data and 600 Å to 5000000Å with Mercury porosimetry will be done. The experimental determination of the adsorption isotherms correlated with an adsorption theory permits to obtain knowledge over the total specific surface area in a porous rock. Usually BET (Brunauer-Emmett-Teller) is used for that. Also, in association with the BJH (Barret, Joyner e Hallenda) approach, the adsorption isotherms allow the determination of the pore size distributions. The Hg porosimetry statistics in combination with the Washburn equation also permits to calculate the pore size distribution of bigger pores. Five samples were investigated in this work originating from dissimilar wells and depth in Brazilian fields. The samples were provided by Cenpes/Petrobrás. The pore size distribution and surface area are parameters related to the material permeability, so several model and empiric equations have already been proposed in order to measure the permeability. In the present investigation, the specific surface area and pore size distribution are used in the Kozeny-Carman equation to predict the absolute cap rocks permeability.

2. THEORY

2.1. Adsorption isotherms

As mentioned previously, adsorption isotherms are adequate for inquiries concerning the spectrum of small pores as in the range of Angstroms (Fernandes, 1990).

Quantities of molar gas adsorbed by a solid at a given temperature as a function of the gas pressure create the adsorption isotherms. By convention, it is usual to express the amount of adsorbed gas being the volume of gas V_o in STP - Standard Temperature and Pressure conditions (0 °C and 76 0torr), whereas the gas pressure is expressed as relative pressure P/P_o , i.e., the relation between the absolute air pressure and the saturation vapor pressure of the gas at the used temperature.

In such an experiment the material actually adsorbed by the solid (the adsorbent) is termed the adsorbate, in contradistinction to the adsorptive which is the general term for the material in the gas phase which is capable of being adsorbed. The adsorption is brought about by the forces acting between the solid and the molecules of the gas (Gregg, 1982).

The theories aiming to describe the adsorption phenomenon were conceived in the 20th century, the Langmuir theory (1918) being pioneer. At present times, the most usual theories are the BET and GAB (Fernandes, 1990). The BET and BJH theories are explained in the following since these were the ones utilized in this work.

2.2. The BET theory

In the BET (Brunauer, Emmett e Teller) theory (1938) occurs physical adsorption of gas on a solid surface and it serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on the surface of pores (considered cylinders) in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer.

The BET equation which describes the amount of adsorbed gas as a function of relative pressure is given by:

$$\frac{V}{V_m} = \frac{C.P/P_o}{(1 - P/P_o)(1 - P/P_o + C.P/P_o)}$$
(1)

where V is the volume of adsorbed gas for each experimental pressure, V_m is the volume of the monolayer recovering the solid surface and C is a constant related to the energetic of the system and is governed by the statistical division of Maxwell-Boltzmann:

$$C = \exp\left[\frac{E_i}{RT}\right]$$
(2)

where E_i is the latent heat of vaporization, R is the ideal gas Constant and T is the Kelvin temperature.

2.3. The BJH (Barret, Joyner and Hallenda, 1951) model

The BET theory treats purely the superficial adsorption phenomena. In a porous framework beyond the superficial gas adsorption the capillary condensation is current. In fact, the amount of gas for a given relative pressure is composed by the volume adsorbed in the walls more than by the capillary-condensed gas in the pore of material. For a given pore

radius as predicted by Kelvin equation (see Fernandes, 1990) there is a critical value for the relative pressure below which exist only adsorbed gas layers and above which the pore is completely filled with capillary-condensed gas.

Many procedures were proposed for calculating the pore size distribution from the N_2 isotherms over the period between 1945 and 1970 (Yang, 2003). The method proposed by Barret, Joyner and Halenda (1951), known as the BJH method, continues to be used today. The BJH approach separates quantitatively the amount of adsorbed gas from the capillary-condensed. Thereby, the following hypotheses are considered:

- The "pore-throat" formation (see Fig. 1) is not present.
- The porous framework is considered to be formed by cylindrical pores with different radii, all pores are nonintersecting.
- Hemispherical meniscus with zero contact angle or complete wetting in the limit of capillary condensation or evaporation.

Hence, the BJH method does not count the hysteresis loop of the isotherm.



Figure 1. Scheme of a "pore-throat" formation, where r_g is the pore throat radius (Fernandes, 1990).

According to Fernandes (1990), the mathematical approach of BJH is concisely explained:

It is supposed that a porous framework with cylindrical pores is exposed to incremental relative pressure, changing P/P_o to $P/P_o + \Delta P/P_o$. When that occurs, a class of pores ranging from radius r to $r + \Delta r$ will be fitted by capillary-condensed gas, in agreement as Fig. 2.



Figure 2. Pore filled by gas (Fernandes, 1990).

That means all pores from this class (*r* to $r + \Delta r$) have a nucleus in their center with radius $r - e_a$ which is able to capture a capillary meniscus for the relative humid $P/P_a + \Delta P/P_a$.

The amount of capillary-condensed gas, $\Delta \theta_{cap}$, is given by:

$$\Delta \theta_{cap} = \frac{\Delta S_r}{2} \left(r - e_a \right) \tag{3}$$

 ΔS_r is defined as the surface area of this class of pores and $r >> e_{a.}$

The pores with radius bigger than this class will have just an increase in the adsorbed layer, since $P/P_o + \Delta P/P_o$ is not enough to incite the capillary condensation, (Fig. 3).



Figure 3. Increase in thickness of gaseous layer adsorbed in the pores which the radius is bigger than $P/P_o + \Delta P/P_o$ (Fernandes).

Supposing that N pores with radius r_o , r_1 , ..., r_{N-1} are the pores whose radii evoked an increase of the thickness of the adsorbed layer, so the volume associated to the addition Δe_a in the adsorbed layer is:

$$\Delta e_{a} = \pi \cdot \left\{ \left(r - e_{a} \right)^{2} - \left[\left(r - e_{a} \right) - \Delta e_{a} \right]^{2} + \dots + \left(r_{N-1} - e_{a} \right)^{2} - \left[\left(r_{N-1} - e_{a} \right) - \Delta e_{a} \right]^{2} \right\}$$
(4)

Considering that the adsorbed layer was assumed to be just a function of relative pressure, independently of radius pore, the Equation (4) can be written as:

$$\Delta \theta_{ads} = \Delta e_a . S(r) \tag{5}$$

where S(r) is the cumulative pore surface with a radius bigger than *r*. Consequently the total increase $\Delta\theta$ related to the incremental $\Delta P/P_o$ will be:

$$\Delta \theta = \Delta \theta_{cap} + \Delta \theta_{ads} = \frac{\Delta S_r}{2} (r - e_a) + S(r) \Delta e_a$$
(6)

In this work, the BET equation as well as the BJH method, are operated in the computational code of the utilized equipment so the dates can be automatically extracted.

2.4. The Kozeny-Carman (K-C) equation

The Kozeny-Carman equation is a widely used relationship for permeability estimates (Schlömer et al, 1997). The equation relates the permeability coefficient (k) to the porosity (ϕ) and the specific surface area (S) of the porous medium according to:

$$k = C_{\phi,S} \frac{\phi^3}{S^2 (1-\phi)^2}$$
(7)

where k is given in $[m^2]$ and S in $[m^2.kg^{-1}]$. The used values for the Kozeny-Carman constant $(C_{\phi S})$ was 5.10⁻¹³ $[m^6.kg^{-2}]$ (Schlömer et al).

2.5. High pressure Hg porosimetry

Mercury porosimetry is built on an observation made by Washburn that the structure of porous solids could be characterized by forcing a nonwetting liquid (Hg) to penetrate their pores. The volume of mercury penetrating the pores can be measured as a function of the applied pressure, from which intrusion/extrusion curves are obtained. The connection to the pore radius distribution is usually made by the Washburn equation (Porcheron et al, 2004):

$$D = \frac{-4\gamma\cos\theta}{P} \tag{8}$$

where D is the pore diameter, γ is the Hg surface tension, θ is the contact angle and P is the applied pressure. A contact angle of 130° and a surface tension of 485dyn/cm (Ross and Bustin) were used. For the present work, the apparent densities and the meso-macro porosities of the samples were calculated using Hg intrusion data.

3. EXPERIMENTAL PROCEDURE

3.1. Material and methods

The five samples used in this investigation originate from dissimilar wells and depth in Brazilian fields. The cap rocks samples were provided by Cenpes/Petrobrás. For confidential matters the samples were named as S1, S2, S3, S4 and S5. The apparent density values were obtained from mercury intrusion data as listed in Tab. 1:

Table 1. Experimental results for apparent density obtained by mercury intrusion of the analyzed cap rocks.

Analyzed samples	Apparent density [cm ³ /g]
S1	2.8677
S2	2.6564
S3	2.7051
S4	2.6832
S5	2.6678

3.2. Hg measurement procedure

Mercury porosimetry was performed to determine the apparent density as well as the meso- and macroporosity of the cap rocks, since porosity values derived from these measurements encompass only the volume of pores with larger equivalent radii (Schlömer et al, 1997).

Specimens from the five cap rocks were desiccated during 24 h at 80 °C. In order to minimize surface effects the measurements were carried out with the maximal amount of material fitted in the penetrometer. The mercury intrusion data was collected on a Micromeritics[®] PoreSizer 9320 Series. The pressure of Hg was increased continuously from 0.003 to 201 MPa and the pore size distributions were determined using Equation (8). According to this equation the radius of pores accessible to mercury intrusion depends on the applied pressure.

The indirect estimate of the total porosity, including the microporosity derived from N_2 adsorption experiments, shall be discussed in the following.

3.3. N₂ adsorption analyses

Nitrogen adsorption at 77 K was done in a Micromeritcs model TriStar 3000 V6.05 utilizing the static volumetric method. A know quantity of pure gas is usually admitted to a confined volume containing the adsorbent maintaining a constant temperature. As adsorption takes place, the pressure in the confined volume diminishes until equilibrium is established. The amount of gas adsorbed at the equilibrium pressure is given as the difference between the amount of gas required to fill the space around the adsorbent, i.e. the dead space, at the equilibrium pressure.

Cap rock samples of 0.7489 \pm 0.2383 g were degassed at 573 K for 3 h, with a residual vacuum of about 50 mTorr. Adsorbed volumes were calculated using the liquid state densities for N₂, 0.808 g/cm³.

The surface area of the samples was determined using the BET isotherm method; a reference monolayer density for this analysis was taken from a range of relative pressures from 0.06 to 0.20. The volume and pore size distribution in the diameter range of 20 Å to 560 Å were obtained by BJH approach using the adsorption isotherm curves.

4. RESULTS AND DISCUSSION

4.1. Isotherms of N₂ (77K)

Figure 4 shows the adsorption-desorption isotherms for N_2 at 77 K. The plots bring the absorbed gas volume per volume of sample (both in cm3) as a function of the relative pressure (*P*/*P*_o). For this calculation the apparent density values (Table 1) measured by mercury intrusion were considered. The close symbols represent the adsorption curves whereas the open ones stand for desorption. Although the five rocks differed in the amount of adsorbed gas their adsorption and desorption curves have a similar shape and did not strictly fall within any IUPAC classification group (Gregg & Sing, 1982). The initial part corresponds to type II, characteristic for non-porous or macroporous adsorbents, and represents unrestricted monolayer-multilayer adsorption. The beginning of the almost linear middle section of the isotherm, is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption is about to begin (Echeverría et al, 1999). However, the hysteresis loop in the multilayer range is a characteristic feature of mesoporous solids, indicating that connectivity has an effect on nitrogen desorption. In addition to the hysteresis due to finite connectivity, there is also a "single-pore" contribution to the hysteresis loops for the five rocks was that the desorption process (Murray et al, 1999). A common feature of the hysteresis loops for the five rocks was that the desorption branch closed at a similar pressure (P/P_o = 0.42). The point of closure is attributed to surface tension of the liquid adsorbed reaching an unstable state at a specific pressure (Echeverría et al, 1999).



Figure 4. N2 adsorption-desorption isotherms for the analyzed cap rocks.

The surface area determination was done using the BET method. The values obtained for S1, S2, S3, S4 and S5 were respectively: $3.2734 \text{ m}^2.\text{g}^{-1}$, $19.2260 \text{ m}^2.\text{g}^{-1}$, $17.4410 \text{ m}^2.\text{g}^{-1}$, $12.4153 \text{ m}^2.\text{g}^{-1}$ and $13.5726 \text{ m}^2.\text{g}^{-1}$. Table 2 compares the surface area values for this work and the values found in the literature. It can be seen that the values are in the same order. Sample S1 presents the smallest value for the surface area and also the least adsorbed gas. This suggests that beyond S1 having a low porosity value it also does not have a big amount of small pores. On the other hand, it is expected S2 has a bigger amount of small pores.

Surface area [m ² .g ⁻¹]	Smallest value	Biggest value
In this investigation	3.2734	19.2260
Yang and Aplin	2.6000	73.1000
Schlömer and Krooss	1.4700	26.7500

Table 2. Surface area values in cap rocks.

4.2. Pore size distributions analyses

Pore size calculations for determination of the total size distribution in cap rocks could be performed with N_2 adsorption isotherm and mercury intrusion (Fig. 5). Just the adsorption curve was chosen because of the hysteresis loop, since pores of a specific size are filled at higher pressures and emptied at lower pressures. The size distribution between approximately 20 Å to 560 Å range was determined with the BJH approach with the adsorption data; the distribution above this range was provided by mercury intrusion. From Fig. 5 it is possible to see that for all samples it was possible to identify a region of mean value of distribution, not having a unique and defined value. Except for S4, all samples have a bigger contribution for the porosity value in the microporous range. S1 presented the smallest cumulative pore volume whereas S4 cumulated the highest amount. The porosity values obtained for the samples are explained on Tab. 3.



Figure 5. Pore size distribution (- -) and cumulative pore volume (symbols) for the investigated cap rocks using N_2 adsorption and Mercury intrusion data.

The curves showed in Fig. 5 provide complementary information where the complete range of pore size distribution is given. Having also the surface area values it was possible with Equation (7) to estimate the intrinsic permeability for the investigated cap rocks. Table 3 shows these results and the morphology characterization for the present work. Table 4 gives the comparison of permeability results and the literature values. As can be seen our estimations using K-C equation are highly agreeing with the values obtained in previous studies.

Table 3. Porosity, permeability and mean pore size data for cap rock samples investigated during this study.

Sample	Depth [m]	N ₂ adsorption	N ₂ adsorption and Hg porosimetry		K-C estimation
		Surface area [m ² .g ⁻¹]	Porosity [%]	Mean pore diameter [Å]	Permeability [m ²]
S1	270	3.2734	2.97	300-500	3.1499x10 ⁻¹⁹
S2	4410	19.2260	4.59	20-100	1.0149x10 ⁻²⁰
S3	4890	17.4410	5.02	50-100	1.2867x10 ⁻²⁰
S4	4410	12.4153	5.55	300000-500000	2.6786x10 ⁻²⁰
S 5	4990	13.5726	4.48	50-100	2.0152×10^{-20}

Permeability [m ²]	Range of values
In this work	$3.1499 \text{x} 10^{-19} - 2.6786 \text{x} 10^{-20}$
Yang and Aplin	$1.8000 \text{x} 10^{-18} - 8.6000 \text{x} 10^{-22}$
Sclömer and Krooss	$4.3250 \mathrm{x10^{-18}} - 1.8000 \mathrm{x10^{-21}}$

Table 4. Values of intrinsic permeability in cap rocks.

5. CONCLUSIONS

To characterize the different ranges of porosity of cap rocks we tried to use complementary experimental techniques and methods of calculation. The combined use of N_2 adsorption and Hg porosimetry together with the BJH approach and the Washburn equation allowed us to obtain a global size distribution of rock porosity.

The cap rocks investigated were essentially mesoporous with volumes between 0.010 and 0.021 cm³.g⁻¹; the maximal range of pore distribution was found for S4 whereas other all samples were in the range 20 - 500 Å.

With the N_2 adsorption isotherm it was possible to calculate the BET surface area and assure the investigation of smaller pore size distributions, since the height of the required pressure for the Hg porosimetry in this pore range could modify the cap rocks structure.

The intrinsic permeability could be estimated by using K-C equation by means of morphological characterization investigated experimentally. The validity of these results can also be studied by using direct permeability measurements.

6. ACKNOWLEDGEMENTS

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