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Characterization of pore systems in seal rocks using Nitrogen Gas Adsorption combined with Mercury Injection Capillary Pressure techniques

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ABSTRACT

Porous microstructure parameters of seal rock samples originating from different depths within Brazilian geological formations were correlated to empirical models which predict the intrinsic permeability. Mercury Injection Capillary Pressure (MICP) and Nitrogen Gas Adsorption (N_2GA) were applied in combination as complementary techniques; MICP to obtain the porosity values and the size distribution of meso- and macropores, and N_2GA associated with the Brunauer, Emmett and Teller (BET) theory to determine the specific surface area (S_o). The Barret, Joyner and Hallenda (BJH) theory was applied to find the size distribution of the micro- and mesopores. The combination of the MICP and N_2GA curves showed that the samples analyzed present a polymodal pore size distribution (PSD) and a total porosity ranging from 0.33 % to 10.44 %. The S_o values measured by N_2GA were higher than those calculated by MICP, due to the majority of the samples having a mean pore size of 20–1000 Å. The intrinsic permeability could also be predicted applying the measured parameters, S_o, PSD curves and total porosity in the Carman–Kozeny and Series–Parallel models. The ranges of permeability values obtained were 4.09×10^{-24}–4.96×10^{-21} m^2 and 9.48×10^{-27}–9.14×10^{-22} m^2, respectively. These results were compared with values reported in the related literature and those obtained for four samples submitted to pressure pulse decay permeability (PDP) tests.

1. Introduction

Seal rocks are geological formations with extremely low porosity and permeability overlying oil or gas reservoirs, which constitute a barrier against the volumetric 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). Seal rock, also called cap rock, is a crucial and sometimes overlooked factor in the evaluation of a potential hydrocarbon accumulation. Together with source rocks, reservoir rocks and overburden rocks, they represent one of the four essential elements of petroleum systems (Hao et al., 2000).

The retention of hydrocarbons by overlying seals is controlled by the capillary entry pressure, the permeability and the extent of diffusive losses (molecular transport) through the fluid-saturated pore space (Schlömer and Krooss, 1997). Today, data on the permeability of cap rock find wide usage in the context of petroleum and gas exploration and also in the storage of anthropogenic CO_2 in the subsurface region, e.g. saline aquifers or exploited gas reservoirs (Hildenbrand et al., 2002). In recent studies, the permeability of seal lithologies was found to range from 4300 down to 0.1 nD (nD = nanoDarcy; 1 nD = 10^{-9} Darcy = 10^{-21} m^2) (Schlömer and Krooss, 1997). Yang and Aplin (2007) measured the vertical permeability of 30 natural mudstones and obtained values ranging from 160 to 0.24 nD. Mallon and Swarbrick (2008) reported values of 148 to 1 nD for the permeability of chalk samples measured using the transient pulse decay procedure.

Cap rocks are formed in the process of sedimentary rock accumulation and so the physical and chemical parameters of these rocks change under the influence of lithogenic processes. In general, the microstructure of cap rocks is highly complex and anisotropic and contains very small-diameter pores (in the order of angstroms). Also, in clastic rocks, like sandstones, pores are observed between compacted grains and in the form of micro- and

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mesoporosity, often attributed to the presence of clays (Padhy et al., 2007). Furthermore, the presence of a wide range of pore sizes makes it impossible to obtain the complete pore size distribution with a single conventional technique. Therefore, cap rock morphology is difficult to characterize, making it necessary to use different methods that are complementary. Previous studies in the literature have been performed with the use of traditional gas methods and helium and mercury porosimetry to establish a combined PSD and porosity determination for coals (Clarkson and Bustin, 1999; Gan et al., 1972; Mastalerz et al., 2008). However, the application of these techniques to characterize the pore system of shales (Bustin et al., 2008; Strapoć et al., 2010) and fault rocks (Janssen et al., 2011) is relatively new.

Many authors have investigated seal rock properties and efficiency through experimental determinations (e.g. Hao et al., 2000; Yang and Aplin, 2007). Nevertheless, the information available on low porosity and low permeability source rocks and seal lithologies is still scarce. Pape et al., 1999, for example, reported that large permeability reductions result from the growth of a minute amount of secondary clay minerals on quartz grains, since this changes the geometry of the hydraulic capillaries. They also noted that it would be very difficult to explain the relationships between the porosity (ϕ) and permeability (k) of different lithologies with a single empirical expression. However, most researchers express k as the product of ϕ and a size parameter for different materials. This size parameter may be, for example, grain diameter, pore radius, or the specific surface area.

In the past few years, in Brazilian oil and gas basins the focus has partially shifted from studying reservoir rocks to obtaining a better knowledge of the pore system of seal rocks. For cores with permeabilities of less than around 0.1 mD, steady-state flow is difficult to achieve in a reasonable laboratory test time (Rushing et al., 2004). It is therefore necessary, besides improving the unsteady-state techniques for permeability measurements, to develop computer-aided methods based on the pore system of seal rocks to predict intrinsic permeability. This task is even more challenging since the complete pore size distribution in seal rock cannot be obtained through applying a single technique as stated above.

In the present work we combined Mercury Injection Capillary Pressure (MICP) and Nitrogen Gas Adsorption (N_2GA) analyses. The former can be applied to investigate the macro- and mesoporous range whereas the latter technique is more suitable for meso- and micropore analysis. Note that according to the IUPAC recommendations (Sing et al., 1985), pores are classified according to their diameter size as micropores (<20 Å), mesopores (20–500 Å) and macropores (>500 Å). The experimental determination of the adsorption isotherms correlated with an adsorption theory provides information on the total specific surface area of a porous matrix (Gregg and Sing, 1982), generally applying the BET theory. In association with the BJH approach, the adsorption isotherms allow the determination of the pore size distributions. The MICP statistics in combination with the Washburn equation allow the calculation of the PSD and of the surface area values for the pores measured considering the work required to immerse a surface in mercury until the applied pressure.

Nine samples originating from four different wells and depths in Brazilian oil and gas fields were investigated in this study. The PSD and specific surface area are parameters related to the material permeability, so several model and empiric equations to assess the permeability have been proposed in the literature. In the present investigation, these parameters are used in the Kozeny–Carman equation (Dullien, 1979) and Series–Parallel model (Childs and Collis-George, 1950; Fernandes et al., 2003; Reznik, 1971) to predict the absolute permeability of cap rocks. In addition, Pulse Decay Permeability (PDP) measurements were carried out on four of these samples for comparison with the predicted results for the seal rock permeability.

2. Experimental section

2.1. Materials

The samples and wells were named according to Table 1. In this table the depth of the respective origin of each sample from the wells and the applied experimental analysis are shown. Figure 1 provides images of the macro- and micro structures for A2, B1 and C1 seal rocks. The scanning electron microscope (SEM) images suggest that the seal rock samples analyzed have an amorphous nature and complex pore shapes with sizes ranging from angstroms to micrometers. Also, the brighter regions are attributed to secondary minerals such as clays on quartz grains, which reduce considerably the porosity and permeability since they change the geometry of the hydraulic capillaries (Pape et al., 1999). Thus, to obtain the conditions required to measure the complete porosity for such a rock type, this paper proposes a combination of the N_2GA and MICP techniques.

The material samples required were obtained from the seal intervals in reservoir sequences. High-quality core material is a prerequisite for the accurate determination of very low permeabilities. All samples were studied applying N_2GA and MICP experiments. In order to compare the permeability values predicted using the parameters obtained in the N_2GA and MICP experimental analysis, and the PDP technique was also used in the case of four of these seal rocks samples, as mentioned above.

2.2. Measurements

2.2.1. Mercury Injection Capillary Pressure

The MICP method is based on the fact that mercury behaves as a non-wetting liquid when in contact with most solids. Consequently, it does not penetrate into the openings and cracks of these substances without the application of pressure. The pressure (P_w) required is a function of the contact angle (θ_{Hg}) of mercury with the porous material to be intruded, its gas/liquid surface tension (γ_{Hg}) and pore radius (r_p). This relationship is given by the Young–Laplace law for the particular case of cylindrical pores as the Washburn equation (Kate and Gokhale, 2006):

$$r_p = -\frac{2\gamma_{Hg}\cos\theta_{Hg}}{P_w} \quad (1)$$

This equation dictates that with increasing pressure, the mercury will intrude into progressively narrower pores for constant values of γ_{Hg} and θ_{Hg}. The volume of mercury (V) penetrating the pores is measured directly as a function of applied

Table 1
Seal rock (SR) samples, sampling depths and wells, type of analysis applied.

Samples	Depth (m)	Well	Experimental analysis		
			N_2GA	MIP	PDP
SR-A1	4412.95	A	x	x	
SR-A2	4413.35	A	x	x	
SR-A3	4415.95	A	x	x	x
SR-B1	4892.05	B	x	x	
SR-B2	4995.95	B	x	x	
SR-B3	4998.25	B	x	x	x
SR-C1	270.90	C	x	x	
SR-C2	1305.20	C	x	x	x
SR-D1	4316.95	D	x	x	x