



The measurement of coal porosity with different gases

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Abstract

Sorption processes can be used to study different characteristics of coal properties, such as gas content (coalbed methane potential of a deposit), gas diffusion, porosity, internal surface area, etc. Coal microstructure (porosity system) is relevant for gas flow behaviour in coal and, consequently, directly influences gas recovery from the coalbed. This paper addresses the determination of coal porosity (namely micro- and macroporosity) in relation to the molecular size of different gases. Experiments entailed a sorption process, which includes the direct method of determining the “void volume” of samples using different gases (helium, nitrogen, carbon dioxide, and methane). Because gas behaviour depends on pressure and temperature conditions, it is critical, in each case, to know the gas characteristics, especially the compressibility factor. The experimental conditions of the sorption process were as follows: temperature in the bath 35 °C; sample with moisture equal to or greater than the moisture-holding capacity (MHC), particle size of sample less than 212 µm, and mass ca. 100 g. The present investigation was designed to confirm that when performing measurements of the coal void volume with helium and nitrogen, there are only small and insignificant changes in the volume determinations. Inducing great shrinkage and swelling effects in the coal molecular structure, carbon dioxide leads to “abnormal” negative values in coal void volume calculations, since the rate of sorbed and free gas is very high. In fact, when in contact with the coal structure, carbon dioxide is so strongly retained that the sorbed gas volume is much higher than the free gas volume. However, shrinkage and swelling effects in coal structure induced by carbon dioxide are fully reversible. Methane also induces shrinkage and swelling when in contact with coal molecular structure, but these effects, although smaller than those induced by carbon dioxide, are irreversible and increase the coal volume. © 2002 Published by Elsevier Science B.V.

Keywords: Coal porosity; Gas compressibility factor; Void volume

1. Introduction

Gas sorption capacity of coal is a rather important issue in coalbed methane prospecting. It contributes to the understanding of both storage and recovery processes.

The gas content of coal has been studied by several authors who concluded that it varies with the characteristics of the coal, such as porosity of macerals, and with temperature and pressure (Mavor et al., 1990; Levine, 1993; Rodrigues and Lemos de Sousa, 1999).

Methane is usually the predominant gas present in a coal seam. However, it is known that several other gases, such as ethane and heavier hydrocarbons [C^{2+}], as well as carbon dioxide, nitrogen, and hydrogen sulphide are also present as revealed by gas chromatographic analysis.

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2. Coal porosity and void volume

2.1. Definitions

Conceptually, *coal porosity* is the volume fraction of coal occupied by “empty spaces”; operationally, coal porosity is the volume fraction of coal that may be occupied by a particular fluid. This varies from fluid to fluid (Levine, 1993).

In its natural state, in the seam, coal also contains inherent moisture (Bed Moisture, moisture-holding capacity—MHC), which occupies part of the pore structure, and the volume fraction free to be occupied by gases in sorption processes corresponds to the so-called *void volume*.

2.2. Classification of coal pores

Different authors have proposed various classifications of pores in coal (Van Krevelen, 1993). However, most of them agree with the classification resulting from high-resolution electron microscopy, as shown in Table 1 (Manual of Symbols and Terminology for Physicochemical Quantities and Units, 1972; McEnaney and Mays, 1989).

In fact, however, coal is characterized by a dual porosity, which consists of micropore and macropore systems. The micropore system is estimated to have pore diameters less than 2 nm, which occur as part of the coal matrix. The macropore system is established by the fracture network that is currently designated by the cleat system (Van Krevelen, 1993). Other discontinuities that contribute to the macropore system are the bedding planes or surfaces. The latter have no important role concerning the gas flow due to the overburden pressure. The different coal porosities have a large contribution to the swelling and shrinkage of coal during

Table 1
Relationship between pore size and coal rank

Pore sizes	Coal rank (ASTM Designation D388-98a)
Micropores $d < 2$ nm	high volatile bituminous coal A and higher
Mesopores $2 \text{ nm} < d < 50$ nm	high volatile bituminous coal (C + B)
Macropores $d > 50$ nm	lignites + sub-bituminous

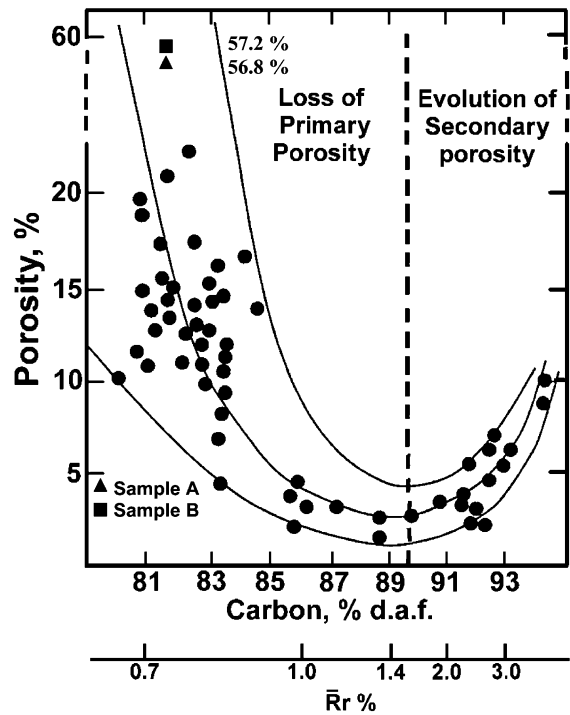


Fig. 1. Relationship between coal porosity and coal rank (after King and Wilkins, 1944, Levine, 1993; modified with data from McCartney and Teichmüller, 1972).

adsorption and desorption processes (Harpalani and Chen, 1997).

Macropores (primary porosity) predominate in lower rank coals (Fig. 1 and Table 1). Geophysical factors, such as compaction and water expulsion, progressively reduce porosity. At about low-volatile bituminous coal rank (ASTM Designation D 388-98a),

Table 2
Methods of coal porosimetry (after Levine (1993), modified)

Major category	Scattering methods	Microscopic methods	Fluid probe methods
Method	low angle X-ray scattering	optical microscopy	volumetric fluid displacement
	electron scattering	scanning electron microscopy	vapor sorption studies heats of wetting
	neutron scattering	transmission electron microscopy	NMR spectroscopy ESR spin label probe

Table 3
Gases used in the experiments

Pure gas	Formula	Molecular diameter (nm)
Helium	He	0.186
Nitrogen	N ₂	0.300–0.410
Methane	CH ₄	0.400
Carbon dioxide	CO ₂	0.510–0.350

the development of secondary porosity begins with the formation of meso- and micropores. This implies an increase of porosity due to well-known progressive changes in the molecular structure through higher ranks.

Porosity is also related to the maceral composition. Vitrinite predominantly contains microporous contents, whereas inertinite predominantly contains meso- and macroporous contents (Gan et al., 1972; Unsworth et al., 1989; Lamberson and Bustin, 1993; Levine, 1993).

3. Methods for measuring coal porosity

Current methods used to determine coal porosity are summarised in Table 2 (Levine, 1993).

Table 4
Rank and maceral composition of samples used in the experiments

Sample	Rr (%)	Maceral analyses (% vol)			
		Vitrinite	Liptinite	Inertinite	Mineral matter
A	0.73	52	5	34	9
B	0.73	78	3	12	7

Rr—mean random vitrinite reflectance.

Regarding “volumetric fluid displacement”, literature only refers to indirect methods based on the determination of He and Hg density (Levine, 1993). Therefore, the novelty of the present investigation is the application of a direct method, based on the measurement of void volume as determined by a sorption process of different gases, using an apparatus for gas sorption isotherm analysis.

4. Experimentation

For the present investigation, we used gases of different molecular sizes (Table 3) to establish their relationship with coal porosity.

The apparatus used for Langmuir sorption isotherms (Fig. 2) was briefly described by Rodrigues and

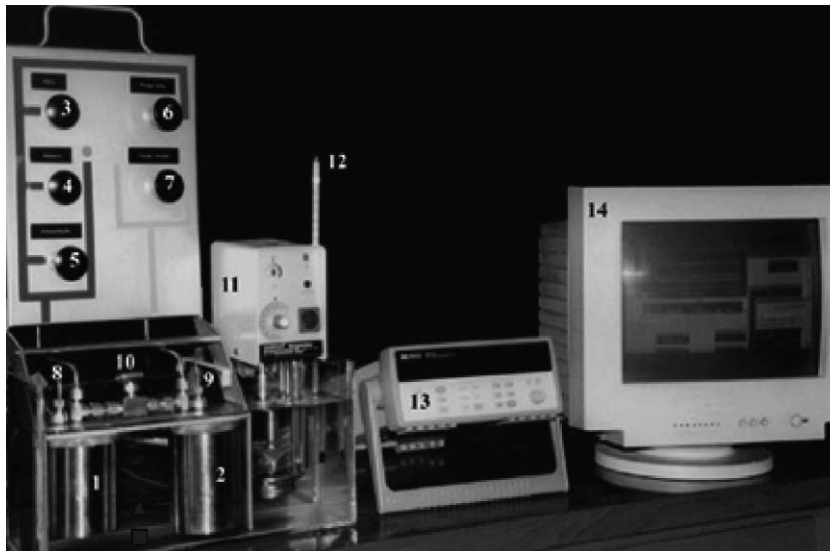


Fig. 2. Apparatus for the determination of gas sorption isotherms by coal. (1) Reference cell, (2) sample cell, (3) helium valve, (4) methane valve, (5) supply valve, (6) purge valve of the system, (7) purge valve of the cells, (8) thermocouple (temperature T_2), (9) thermocouple (temperature T_3), (10) connection valve between cells, (11) thermostatic head, (12) thermometer (T_1), (13) voltmeter, (14) computer with software to perform the data acquisition.

Table 5
Experimental conditions

Sample	Mass (SC+M) (g)	T (°C)	MHC (%)	M (%)	Pressure (bar)
A	115.66	35	3.7	18.1	<2
B	115.56	35	3.2	18.6	<2

SC—sample coal; M—moisture in the analysis sample; MHC—moisture-holding capacity.

Lemos de Sousa (1999) and Rodrigues et al. (1999). With regard to this device and the experiments that were performed, it should be noted that the apparatus (Fig. 2) was designed based on the volumetric techniques that use gas expansibility, based on Boyle's Law of ideal gases, to perform the measurements of adsorbed gas. As adsorption isotherm characteristics significantly change, depending on the temperature level, it is necessary to keep the system in a constant temperature bath (T_1) at ± 0.01 °C.

The equipment has a set of different valves (supply, purge, connection, and security), piping to permit gas flow (this piping can hold pressures up to 20 MPa), and two cells—the “reference cell” (where pressure can reach 17.5 MPa), and the “sample cell” (maximum pressure of 7 MPa). The method implies that all results are calculated on the basis of volume determinations. The reference cell has a volume of ca. 100 cm³ and the sample cell, ca. 200 cm³. However, due to the accuracy of the method, all volumes must be calculated with the precision of $\pm 10^{-4}$ cm³. The temperature of the cells is controlled by thermocou-

ples (“reference cell”— T_2 , “sample cell”— T_3). In fact, the smallest variation in temperature implies changes in the cell pressure.

Pressures in both reference and sample cells (P_1 and P_2) are independently monitored by high-precision pressure transducers.

All the time-dependent temperature and pressure data are fed into a computer with an acquisition plate of 20 channels “Armature Multiplexer Module” associated to a voltmeter with a resolution of ± 10 μ V.

The main characteristics of the tested samples are shown in Table 4. It should be noted that these samples have the same rank, similar liptinite, and mineral matter contents, as well as the same MHC value. Therefore, relevant differences in the characteristics of the coals are primarily, and intentionally, restricted to the vitrinite versus inertinite contents.

4.1. Experimental conditions

The specific experimental conditions used for the experiments are shown in Table 5. The following should also be noted.

- The moisture content of the test samples for sorption isotherms is irrelevant, provided that it is equal or greater than the MHC, as demonstrated by various authors including Ruppel et al. (1972) and Rodrigues and Lemos de Sousa (1999).

- Pressure was chosen in order to avoid variations in the compressibility factor effect. In fact, it is well known that all gases at pressures up to 0.2 MPa have

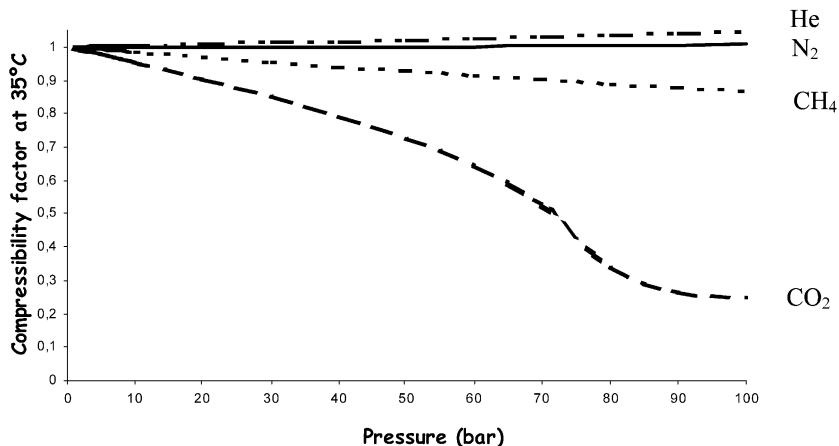


Fig. 3. Compressibility factor of the individual gases at 35 °C.

Table 6
Measurement of empty “sample cell” volumes

Gas	Volumes (cm ³)
He	195.12 ± 0.40
N ₂	195.02 ± 0.40
CH ₄	194.92 ± 0.50
CO ₂	194.92 ± 0.40

almost the same compressibility factor value (Fig. 3). Therefore, for the current investigation, pressure was kept below 0.2 MPa.

- The system was kept in a constant temperature bath at 35.00 ± 0.01 °C.
- The weight of the samples was ca. 100 g crushed to a particle size less than 212 μm.

5. Results and discussion

Irrespective of the gas that was used, volume measurement of the empty “sample cell” of the apparatus is the same (Table 6). In fact, in such a case, gases are not in contact with the coal sample.

Due to its small molecular diameter and the absence of reaction with coal, helium is considered to be the only gas that gives a precise measurement of the void volume (Mavor et al., 1990). Therefore, the results in Tables 7 and 8 are interpreted as follows.

5.1. Measurements with He

The higher void volume of sample B compared with sample A corresponds to higher vitrinite content (Table 4). When He is used to measure the void volume, there is no coal shrinkage in the desorption process since it is a non-adsorptive gas, as confirmed by values listed in Table 8 showing that there are no significative variations in the results from the first test to the third.

Table 7
Average of “void volumes” with different gases

Sample	Gases (cm ³)							
	He	N ₂	N ₂ /He	CH ₄	CH ₄ /He	CO ₂	CO ₂ /He	CO ₂ /CH ₄
A	110.76 ± 0.40	117.87 ± 0.30	1.06	146.78 ± 1.00	1.33	288.56 ± 1.20	2.61	1.97
B	111.62 ± 0.30	119.80 ± 0.30	1.07	143.93 ± 1.10	1.29	269.36 ± 1.30	2.41	1.87

5.2. Measurements with N₂

Although the same general interpretation as the one above applies in this case, the main difference between the results of the two samples is due to the recognized affinity, albeit small, of N₂ for coal structure.

5.3. Measurements with CO₂ and CH₄

It is well known that these gases have a greater affinity with coal structure (mainly vitrinite) than He and N₂, in terms of the interaction of intermolecular forces (Van der Waals and hydrogen bonding) (Levine, 1993; Van Krevelen, 1993).

This also explains the higher void volume obtained for sample A than for sample B. It is noted that the void volume determined with CO₂ is ca. twice as much as the one determined with CH₄.

The results shown on Table 8 confirm that swelling induced by adsorption process as well as the shrinkage resulting from desorption of carbon dioxide are reversible and do not modify the coal structure. It is also possible to observe some “abnormal” negative values in coal volumes, which result from the great affinity of CO₂ for the coal structure. Since this method measures the volumetric relationship between the stored and the free gases in coal, the obtained results also confirm that a great quantity of CO₂ is retained on coal structure.

The methane sorption process also induces swelling and shrinkage in coal but, in this case, both are irreversible processes, which depend on the rank and moisture of the coal. However, our results (Table 8) demonstrate that the void volume decreases from the first experimental test to the third one, which is explained by the increase of coal volume induced by methane.

The progressive increase of the N₂/He, CH₄/He, and CO₂/He ratios conforms with the increase in

Table 8
Measurement of “coal volumes” (V_c) and “void volumes” (V_v) with different gases

Sample	Experimental tests	Gases (cm ³)							
		He		N ₂		CH ₄		CO ₂	
		V_c	V_v	V_c	V_v	V_c	V_v	V_c	V_v
A	1	80.83	114.29	77.21	117.81	47.57	147.34	– 94.11	289.03
	2	81.11	114.01	76.92	118.1	47.73	147.18	– 92.44	287.36
	3	80.63	114.49	77.32	117.7	49.18	145.74	– 94.38	289.3
B	1	83.37	111.75	75.22	119.8	46.53	148.39	– 75.52	270.44
	2	83.6	111.52	75.41	119.61	50.98	143.94	– 73.44	268.36
	3	83.55	111.57	74.98	120.04	55.46	139.45	– 74.35	269.27

affinity of N₂, CH₄, and CO₂ for the coal structure. Furthermore, in considering the CO₂/CH₄ ratio, we verified that the CO₂ affinity for the coal structure is ca. twice as much as that of CH₄, even for pressures under 0.2 MPa. This clearly confirms and explains why coalbed methane (CBM) prospecting is enhanced by injecting CO₂ in wells under pressure (Van der Meer, 2000), since CH₄ is the major and most important component of CBM.

6. Conclusions

The measurement of coal porosity with different gases is a very complex subject in which both the size of the gas molecules and their relationship with the coal structure have to be taken into account.

The present study aimed at understanding the relationship between the gases used to investigate the coal porosity and the induced swelling and shrinkage of coal structure. In our opinion, this is an important issue to be considered in the coalbed methane prospecting and production, since the referred parameters can dramatically induce changes in coal permeability.

Since He is the gas with the smallest molecular size, it is expected to permeate, more successfully, the entire coal structure and, therefore, permit a more precise measurement of the void volume.

The fact that the same volume was obtained for the empty “sample cell” when using different gases (Table 6) leads to the conclusion that differences in void volume (Table 7) are a result of the relationship between coal structure and gas. If we consider He to be the gas that gives the standard measurement, then the following ranking in affinity to the coal structure is verified: N₂ > CH₄ > CO₂.

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