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CO$_2$ AND CH$_4$ DISPLACEMENT SORPTION IN MEDIUM RANK GRADE COAL UNDER LOW GAS PRESSURE

WYMIENNA SORPCJA CO$_2$ I CH$_4$ NA WĘGLU KAMIENNYM O ŚREDNIM STOPNIU METAMORFIZMU W ZAKRESIE NISKICH CIŚNIEŃ GAZÓW

The paper presents a study of the sorption /desorption kinetics and equilibrium states with displacement of sorbate gases, as well as the dilatation/ contraction of coal accompanying the sorption processes under low pressures of the gases. In order to find a correlation between the properties of hard coal and the process of methane liberation in the course of time. Based on the results obtained it seems worth stressing that there exists a need to carry out parallel sorption dilatation studies as part of the structural study of hard coal.

Key words: gas sorption, coal, dilatation/contraction, CO$_2$, CH$_4$.

W prezentowanej pracy przedstawiono wyniki badań kinetyki i statyki procesów sorpcji CO$_2$ i CH$_4$, przy zmianie kolejności sorbowanych gazów oraz rozszerzania/kontrakcji węgli towarzyszącym procesom sorpcyjnym w zakresie niskich ciśnień gazów. Celem pracy jest znalezienie powiązań pomiędzy właściwościami węgli kamiennych, a przebiegiem procesu uwalniania metanu. Na podstawie uzyskanych wyników stwierdzono konieczność prowadzenia równolegle badań sorpcyjno-dylatometrycznych w przypadku badań strukturalnych węgli kamiennych.

Słowa kluczowe: sorpcja gazów, węgiel kamienny, rozszerzalność/kontrakcja, CO$_2$, CH$_4$.

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1. Introduction

The sorption on coal of single substances of low molecular weight has drawn relatively much attention of physical chemists (Ceglarska-Stefańska, 1998; Milewska--Duda et al., 1995; Weishauptova et al., 1998; Ceglarska-Stefańska et al. 1993, Larsen et al., 1995). Nevertheless, the complexity of the physical and chemical nature of coal renders difficult the interpretation and prediction of the changes of the coal sorption for these substances (within a wide range of sorbate pressures). The results of physical, chemical, and structural investigations, including a wide spectrum of sorption studies, have lead to the conclusion that there is no possibility of describing the organic structure of the substance of coals differing in their degree of metamorphism only with a single model — one formula. Therefore many authors present results of investigations relating to the structural changes of coals occurring during the metamorphic processes. It is commonly accepted that the sorptive capacity of coals is determined by the degree of metamorphism (the chemical nature of the organic coal substance, its porosity and the rigidity of its structure) as well as by its petrographic composition (Ceglarska-Stefańska, 1998; Milewska-Duda et al., 1995; Weishauptova et al., 1998).

In addition it should be noted that the sorption studies play a special role to extend knowledge about the accumulation and behaviour of mine gases within the coal beds. On the other hand, studies of desorption of the mine gases; in particular, their dominant component, methane, remain an important subject area. They are related to the evolution of methane in old workings and its extraction from non-exploited beds, as well as for ecological reasons (e.g. the reduction of CO_2 emission to the atmosphere). In gas-containing coal beds there is a migration of gases from the deeper beds containing a higher gas concentration to the upper beds close to the operational area. It is also known that the volume and distribution of the coal pores are one of the factors determining the extent and ease of methane diffusion from the porous structure, during mining exploatation. For this reason, new techniques of obtaining methane from the beds require a much more detailed description of the system (coal/methane), than the estimation of the coal sorption capacity. For all these reasons the question of predicting the methane recovery from the coal beds, based on the known sorptive and diffusive properties of coals, obtained from the investigations of the displacement sorption of CO_2, CH_4 and their mixtures is important. In order to find the correlation between the properties of the hard coal and the course of the process of affecting methane liberation, as well as to find the factors determining the speed of the latter process we have initiated investigations of the sorption/desorption kinetics and equilibrium states with displacement of sorbate gases, as well as dilatation/contraction of coal accompanying the sorption processes under low gas pressures (the first stage). Primarily this work gives the basic information on the displacement sorption, which has not yet been satisfactory analysed. Therefore, each new piece of information is interesting both for the theory and its possible practical use.

2. Experimental

The low-pressure sorption investigations were carried out using volumetric methods, under isothermic-isobaric conditions, at 298 K (Ceglarska-Stefańska et al., 1993). Coal samples from the KWK Moszczenica Mine; bed 510/1-2, were studied. Their characteristics and petrographic analysis are summarised in Tables 1 and 2.

TABLE 1

Short characteristics of the coal

Parameters		
Ash	[wt%]	4.96
V^{daf}	[wt%]	22.32
C^{daf}	[wt%]	90.12
H^{daf}	[wt%]	4.67
d_{He}	[g/cm^3]	1.34
Porosity	[%]	4.50

TABLE 2

Petrographic analysis of studied coal

Group of macerals	Maceral	[%]
Vitrinite	Tellinite	4.6
	Collinite	31.9
	Vitrodetrinite	—
	Colodetrinite	27.2
Liptinite	Sporinite	3.2
	Cutinite	—
	Resinite	0.1
Inertinite	Fusinite	10.9
	Semifusinite	7.7
	Sclerotinite	0.9
	Macrinite	1.8
	Micrinite	4.8
	Inertodetrinite	6.6
Mineral substance		0.8

The characteristic feature of this coal is the presence of numerous fissures and in its structure. Some of the fissures are visible to the naked eye, others under a microscopic examination, some are empty, some are filled with pyrite, and yet

others are only partially filled with pyrite. Smaller fissures have formed after the crystallisation of the mineral.

The sorption investigations were carried out using powdered coal of grain size of $\varphi = 0.001-0.0015$ m and plates of $0.015 \times 0.015 \times 0.05$ m in size, cut off the lump. The latter had tensometers attached parallel and perpendicular to its stratification, to enable the changes of the external coal sample dimensions accompanying the sorption process. Prior to the experiments the coal samples were degassed down to 10^{-5} hPa, for about 70 hours. Then, helium was supplied to the system, so as to remove any gas molecules from the coal micropores, and after 48 hours the system was again degassed to 10^{-5} hPa, and until readings on the resistance gauge remained constant. The sorption kinetics and the variations of the external dimensions of the samples were determined for carbon dioxide, methane and their mixture (51.8% CO_2 and 48.2% CH_4) as the sorbates. These gases play an important role in the process of gas liberation in various technological processes and mining techniques. Moreover, they considerably differ in their physical and chemical properties (Poradnik fizykochemiczny, 1974), which gives a significant differentiation of the sorption capacity and the velocity of the sorption process in hard coals (Weishauptova et al., 1998; Ceglarska-Stefańska et al., 1993; Marecka 1999). In this paper the displacement sorption was determined for the following systems:

A) coal — CO_2 presorption — CH_4 sorption,
B) coal — CH_4 presorption — CO_2 sorption,
C) coal — sorption of the mixture of CO_2 and CH_4.

3. Results and discussion

A) c o a l — C O$_2$ p r e s o r p t i o n — C H$_4$ s o r p t i o n

CO_2 was supplied to the measuring system in portions, up to 458.3 hPa. It may be reasonably assumed that for the lowest pressure of added CO_2, the gas molecules locate in the sorption space of the coal sorbent by adsorption. This suggestion finds confirmation in the lack of changes of the outer dimensions of the coal. Afterwards, methane was supplied to the coal/CO_2 system, at a pressure of 543.9 hPa. Introduction of methane, after the presorption of carbon dioxide, caused desorption of the mixture of gases. This effect was observed both for the plates and grains of coal (Fig. 1 a, 1 b). The gas desorption was accompanied by a significant contraction of the coal samples. This experiment was conducted over a long time-period, even up to 150 hours, because of considerable disturbances of the kinetics of the variations in the coal's dimensions, indicating that equilibrium has not been reached in the system. It may be assumed that the introduction of methane caused a reduction of the initial partial pressure of CO_2 in the sorption space. Therefore, particularly at the initial period of the contact of coal with the gases (CO_2 and CH_4) carbon dioxide was desorbing, which caused the hard coal to contract

(Fig. 2). For this reason less methane adsorbed on the surface of the pores expanded due to CO_2 sorption, as well as in mesopores and macropores. The majority of the methane filled the pores as a free gas. This fact finds confirmation in published literature data, concerning the explosions of "unsaturated" beds. One of the possible explanations of this phenomenon is the presence of significant amounts of sorbate of higher sorption ability (for instance CO_2) than methane in the beds (Close et al., 1992). At a subsequent, higher value of the pressure of supplied methane, no gas desorption was observed. On the other hand, the sorption of the
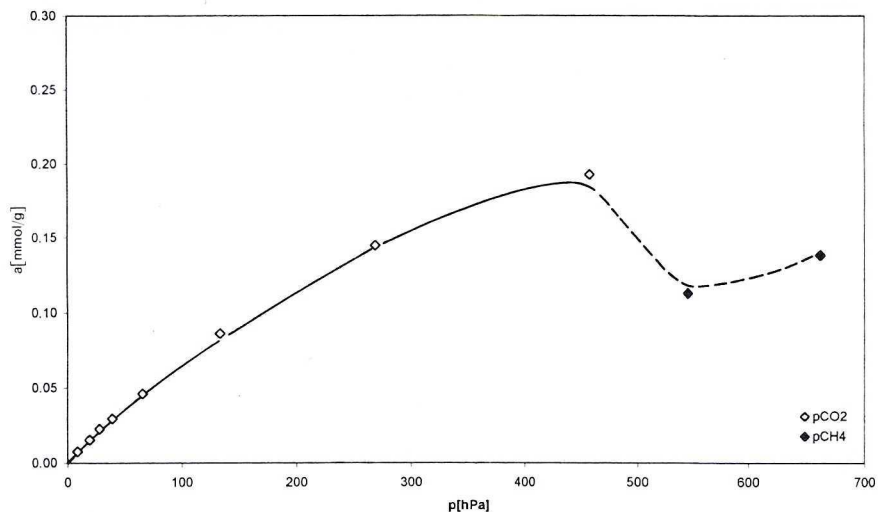
Fig. 1 a. Sorption capacity of coal towards CH_4 after CO_2 presorption, box
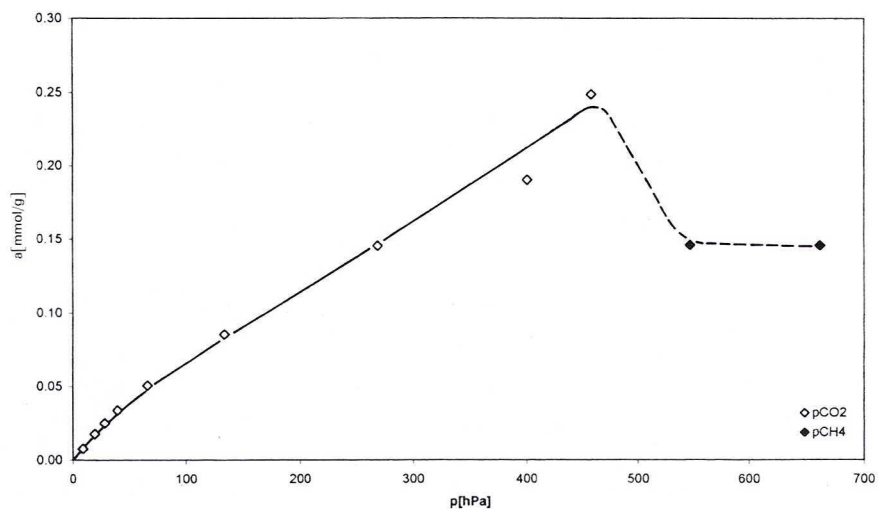
Fig. 1 b. Sorption capacity of coal towards CH_4 after CO_2 presorption, grain

mixture of CO_2 and CH_4 was insignificant, which was also confirmed by the run of the kinetics of the coal dilatation. In situ, both effects should influence changes of the bed's permeability.
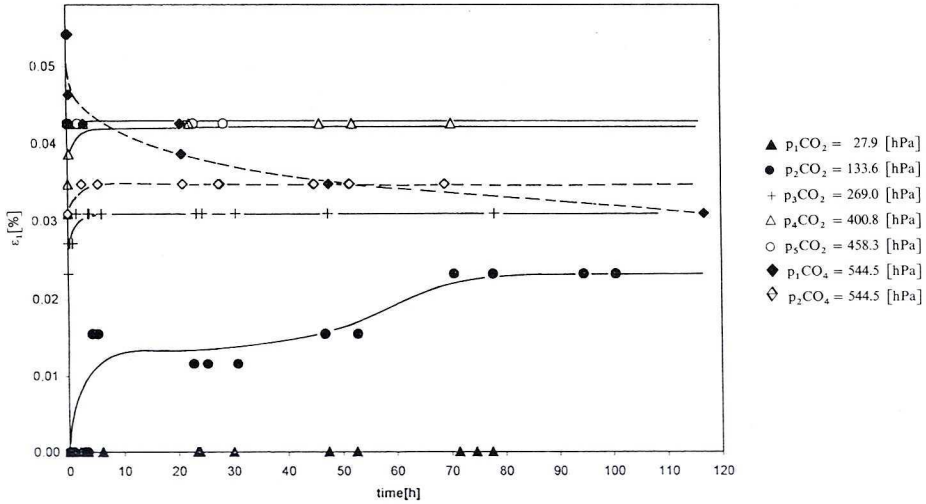

Fig. 2. Kinetics of coal dilatation for the system A

B) coal — CH_4 presorption — CO_2 sorption

In this system the sorption of methane was carried out initially, up to a pressure of 277.7 hPa. No dilatation of the studied coal samples was observed over the range of methane pressures varying from 0 to 277.7 hPa. Afterwards, carbon dioxide was supplied under a pressure of 573.2 hPa. It may be seen on the curve of the sorption isotherm (Fig. 3 a, 3 b) that the introduction of CO_2 to the system did not cause any desorption of the mixture of gases. On the contrary, an increase of $a = f(p)$ was observed. Methane was accumulated on the surface of the coal, most probably in a mono--layer, by physical adsorption. Only after prolonged contact with CH_4 with the coal, and at higher gas pressures, methane molecules penetrated the coal structure, due to sorbate diffusion in the molecular and elastic absorbing phase and because of the relaxation of the chains. On the other hand, carbon dioxide molecules, of sufficiently small dimensions (a critical diameter of 0.28 nm), and activation energy, penetrated pores inaccessible to other gases. Under the conditions of our experiment this effect is a result of the more easy penetration of the coal structure, broadened by methane molecules, by the carbon dioxide molecules. It is commonly known that the displacement of the sorbate molecules by small molecules facilities penetration of some of the previously closed micropores (Close et al., 1992; Radovic et al., 1997; Smith et al., 1987).
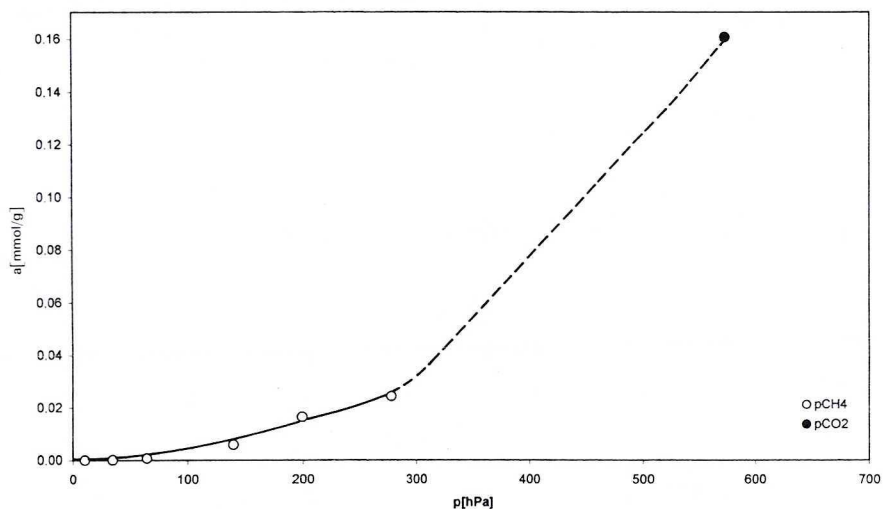
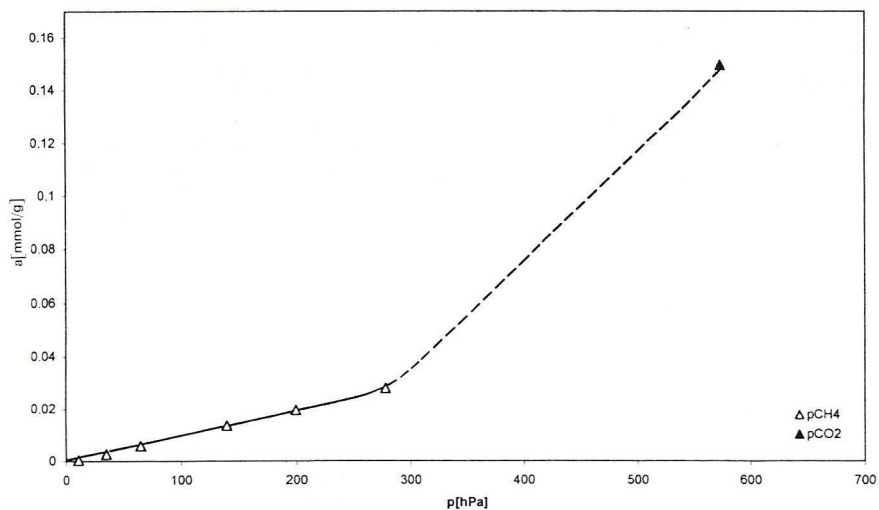Fig. 3 a. Sorption capacity of coal towards CO_2 after CH_4 presorption, box

Fig. 3 b. Sorption capacity of coal towards CO_2 after CH_4 presorption, grain

C) coal — sorption of the mixture

Sorption isotherms of the mixture of gases were described using the Langmuir isotherm, extended to the two-component gas mixtures by Markham and Benton (Paderewski, 1999). From the equation given below it results that the adsorption of any of the components of the binary mixture of gases increases with the increase of the partial pressure of this particular component and a decrease of the partial pressure of the second component:

$$a_1 = \frac{a_{m,1}b_1p_1}{1+b_1p_1+b_2p_2},$$

$$a_2 = \frac{a_{m,2}b_2p_2}{1+b_1p_1+b_2p_2}.$$

The total adsorption of both components is equal to:

$$a = a_1+a_2,$$

where a_1 and a_2 denote adsorption values for single components of the binary mixture, $a_{m,1}$, $a_{m,2}$, b_1 and b_2 —empirical constants, p_1, p_2 — partial pressures [hPa].

The course of the sorption isotherm of the mixture of gases (CO_2 and CH_4), both for the grain fraction and the box does not indicate any disturbances in the coal structure (Fig. 4 a, 4 b). On the other hand, the kinetic runs of the dilatation of the studied samples, during the sorption of the mixture of both gases, showed deviations from the above relationship over the whole range of the pressures studied (Fig. 5). This fact may be explained by the blocking of the fissure-like and conical pores by methane (on the basis on an X-Ray radiography test), making the access of CO_2 to the pore net more difficult, or by the activated diffusion of both gases at the temperature of the experiment (Mahajan, 1991; Walker et al., 1999). The opinion that the distance from the equilibrium state is dependent on the ability of the particular sorbate for overcoming the energetic barrier, related to the diffusion by the narrowed ultramicropores (0.6–0.7 nm) is equally commonly held. It is also known that the narrow entrace holes to the
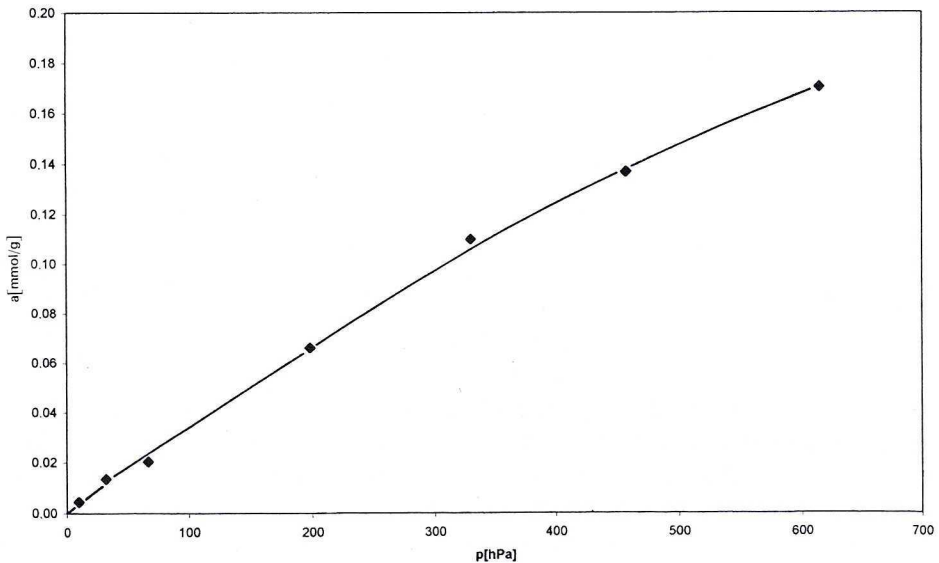

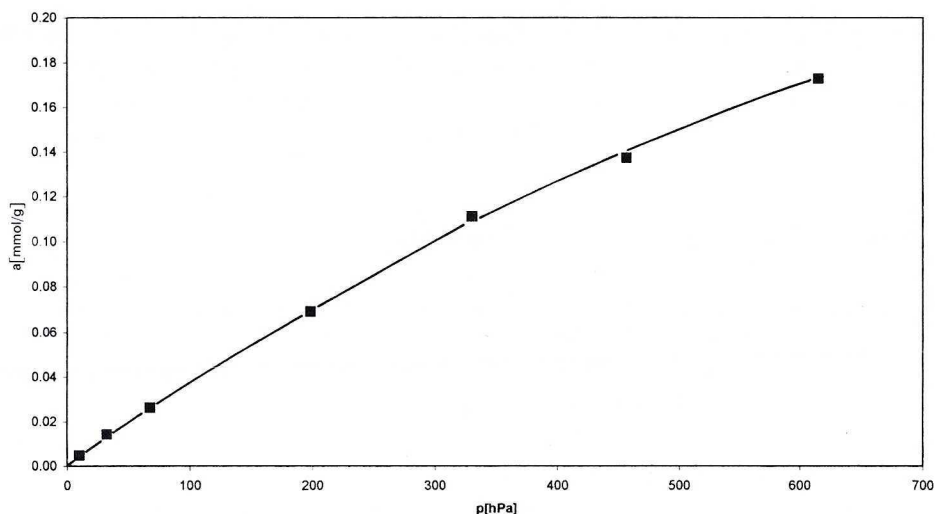Fig. 4 a. Sorption capacity towards the mixture of gases, box

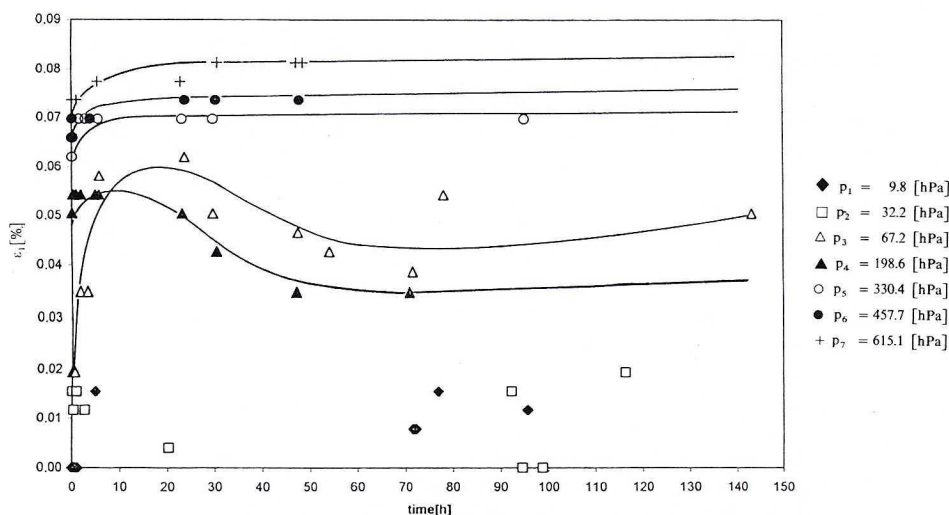Fig. 4 b. Sorption capacity towards the mixture of gases, grain

Fig. 5. Kinetic run of the coal dilatation for the system C

micropores in hard coals are comparable with the dimensions of the methane molecules (Walker et al., 1999) and this gas needs some more time to penetrate the whole sorption space, which is necessary to attain equilibrium. On the contrary CO_2 molecules may have easy access to all pores with a radius greater than 0.271 nm and therefore only carbon dioxide penetrates the ultramicropores perfecty.

It should also be remembered that the presence of the interconnected, but very narrow system of pores imposes serious limitations for the application of the sorption data for the evaluation of the content of methane in the coal bed and for the

possibility of its recovery. The dilatation investigations carried out show that even small amounts of carbon dioxide might influence the bed permeability. This should be taken into account in the search for a strategy for methane recovery and making use of non-conventional sources of this gas.

4. Conclusions

• The structure of the coal studied, containing fissures and cracks, is responsible for its low sorption capacity and the negligible dependence $a = f(p)$ on the grain-size distribution in the systems studied. It also determines a relatively good accessibility of the penetrated structure to the spherical molecule of methane.

• The presence of methane molecules in the coal/CO_2 system causes desorption of CO_2 from the samples and contraction of coal, as well as a reduction of the coal sorption capacity towards the gaseous mixture (CO_2 and CH_4) rather than towards CO_2.

• Based on the results obtained from the low pressure investigations is seems worth stressing that there exists a need to carry out parallel sorption/dilatation studies in structural studies of hard coal. There will be further research into coal with various petrographic components and different quantity of mineral substances.

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