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DISPLACEMENT SORPTION OF CO_2 AND CH_4 ON LOW RANK HARD COAL, WITHIN A LOW GAS PRESSURE RANGE

WYMIENNA SORPCJA CO₂ i CH₄ NA WĘGLU KAMIENNYM O NISKIM STOPNIU METAMORFIZMU W ZAKRESIE NISKICH CIŚNIEŃ GAZÓW

The study of the sorption/desorption kinetics and equilibrium states of single CO_2 and CH_4 gases, mutually displacing an earlier sorbed one, as well as the studies of coal dilatation/contraction accompanying the sorption processes under low gas pressures are presented in this paper. The aim of the work was to find the correlation between the properties of the hard coal and the progress of the process of methane liberation. Based on the results obtained it seems worth stressing that there exists a need to carry out parallel sorption/dilatation investigations during structural studies of hard coals. Moreover, the results of the sorption investigations may be used for the analysis of the stress in exploited rock masses.

Key words: gas sorption, coal, dilatation/contraction, CO2, CH4

W prezentowanej pracy przedstawiono wyniki badań kinetyki i statyki procesów sorpcji: pojedynczych gazów 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 oraz wykorzystania wyników badań sorpcyjnych do analizy naprężeń w górotworze podczas eksploatacji górniczej.

Słowa kluczowe: sorpcja gazów, węgiel kamienny, rozszerzalność/kontrakcja, CO2, CH4

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1. Introduction

The sorption of gases by coal is a very important area of investigation, among others leading to the improvement of the process of gas recovery from coal beds and to a better understanding of the phenomena associated with the presence of gases in a coal mine. The process of carbonization on a geological time-scale results in the formation of solid matter and gaseous products entrapped within the porous structure of the coal-beds, because of their spatial isolation and enclosure. This phenomenon is responsible for a characteristic feature of the majority of bituminous coal beds — the presence of "so-called" mine gases in the coal's porous structure. The majority of coal beds contain methane and carbon dioxide. Methane, formed during the carbonization process and carbon dioxide — often introduced into the bed by the intrusion of magma, in close contact or nearby interaction and effect upon the coal bed.

The presence of these gases in the pores of the coal substantially affects the stress and deformation of the coal. The gases may be present in the form of free or sorbed gas, and their ratio depends on the temperature and pressure in the coal bed. The quantity of sorbed gas depends additionally upon such properties of the coal as: its quality, porosity, humidity or content of mineral substances. On the other hand, the pressure of the free gas and surface forces determine the effective stresses (Harpalani, Chen 1993).

The investigation of the structure of coal involves studying the structural variations of the organic coal matter. Such variations may be caused, among the others, by the sorption of gases and vapours, when the carbon matter swells and its strength parameters change. The sorptive capacity of coal is responsible for its volumetric deformation and the reduction of its surface energy, and this way for the reduction of the rock's resistance and a further increase of its deformation. It is of a particular significance during coal exploitation in gas-containing mines, because the volumetric changes may affect the nature of the stresses in the rock mass (Ceglarska 1998; Milewska-Duda, Duda 1995; Weishauptowa, Medek 1998).

Models of gas flow in the beds indicate that the gas emission to the excavation is significantly affected by the permeability of the bed and of the neighboring rocks and by the rate of gas desorption. However, the effect of three basic factors: stress, gas content and the physical and chemical properties of coal, is also important. The sorption of single substances of low-molecular weight in hard coal has been extensively studied. Nevertheless, the complexity of the physico-chemical nature of these sorbents makes the interpretation and prediction of changes of the sorptive properties of these substances difficult (Ceglarska-Stefańska 1993; Żyła et al. 1991; Jodłowski 1999). Therefore the relationship between the gas sorption by the coal and the physical and chemical properties of this coal, dependent on its quality, is not clearly defined in the literature. The data in the literature show some correlation between the petrographic composition of the coal and its ability to burst out and cause the liberation of the gases. Coals with a high content of macerals from the inertite group (particularly — fusinite and semi-fusinite) emit gases more slowly, which corresponds to a higher susceptibility to bursting out (Ceglarska-Stefańska 1993; Larsen et al. 1995). Not only the problem of outbursts but also the

recovery of methane from coal beds as an additional energy source is of importance. The data shows that the problem is the subject of search for and prediction of optimal output under these particular conditions. Therefore the authors of this paper have attempted to discover a correlation between the properties of hard coal and the course of methane liberation and to define the factors determining the velocity of this process. This was achieved by studying the sorption/desorption kinetics and equilibrium states accompanying the change of sorbed gases, as well as dilatation/contraction of coals accompanying the sorption processes under low gas pressures. The studies also involved the displacement sorption of CO_2 and CH_4 and their mixtures by hard coals. Some of these results have already been published earlier (Ceglarska-Stefańska, Zarębska 2001). The deep interest in the questions being studied led the authors to continue investigations on the coals of lower rank. The last-mentioned paper also contained the mathematical derivation of formulae used to calculate the quantity of sorbed gas (*a*).

2. Experimental

The low-pressure sorption studies were carried out using the volumetric method, under the isothermal-isobaric conditions, at 298 K (Ceglarska-Stefańska 1993).

The technique applied made possible the studyof the sorption kinetics (CO₂ and CH₄) on the hard coal, with simultaneous determination of the kinetics of dilatation (for samples in the form of plates), gradually, i.e. under the progressively increased sorbate pressures. The quantity of the sorbed substance is calculated from the equation of the gas state, taking into account the mass balance of the dosed and non-adsorbed gas (Ceglarska-Stefańska, Zarębska 2001). Based on the data on the equilibrium sorption processes the sorption isotherm, the most popularly recognised relationship in sorption studies, was drawn. The subject of studies was a hard coal from the Hard Coal Mine KWK Brzeszcze, bed 325, level 430 meters. Its shortened characteristics and petrographic analysis is depicted in Tables 1 and 2.

The X-ray investigations show that this coal contains macerals, a considerable amount of the clayey mineral substance and a small amount of pyrite. Telinite does not generally contain pores and the openings of the cells are closed with gelinite. The important maceral is fusinite, present in two forms. One of them is pyro-fusinite, of a yellow appearance, with thin walls, very brittle, with numerous empty TABLE 1

Short characteristics of the coal

TABLICA 1

Charakterystyka badanego węgla

Param	eters [%]			
W ^a	2.9 15.5			
A ^a				
V ^{daf}	40.87			
C^{daf}	79.6			
H ^{daf}	5.0			
O ^{daf}	13.1			
N ^{daf}	1.6			
S ^{daf}	0.7			
Aton	nic ratio			
H/C	0.75			
O/C	C 0.12			
N/C	/C · 0.017			
S/C	S/C 0.003			

Petrographic analysis of studied coal

TABLICA 2

Group of macerals	Maceral	[%]	
Vitrinite	Tellinite	1.3	
	Collinite	16.1	
	Vitrodetrinite	0.9	
Liptinite	Sporinite	7.9	
	Cutinite	0.7	
	Resinite	0.6	
Inertinite	Fusinite	10.6	
	Semifusinite	4.4	
	Sclerotinite	2.2	
	Macrinite	0.7	
	Micrinite	0.7	
	Inertodetrinite	4.0	
Mineral substance		9.5	

Analiza petrograficzna badanego węgla

Reflection $R^{\circ} = 0.6769\%$.

openings of the cells, which very often appears in small fragments. Fusinite is frequently impregnated with pyrite. Semi-fusinite is less common. Some parts of its cell openings are also empty. Some sclerotynite, particularly sclerotia and the plectenchymatic tissue of fungi exhibit empty spaces. For colotelinite small local fissures, remaining from the cellular structure are a characteristic feature.

Table 1 contains the elemental analysis and the appropriate atom proportions. The value of H/C ratio, shows the presence of molecular binding in the studied samples of coal (aliphatic binding), while a high O/C ratio and the content of O^{daf} indicate the oxygen-functional groups from one side, or the presence of non-reactive oxygen. This is also confirmed by the water vapour and methanol sorption studies (Krzyża-nowski et al. 2001).

The sorption investigations were carried out on grain fractions ($\phi = 1-1.5$ mm and below 0.05 mm, and on the plate ($15 \times 15 \times 5$ mm), cut from the coal lump. Tensometers, glued to the surfaces of sections measured the variations of the outer dimensions of the coal samples, accompanying the sorption (|| parallel and perpendicularly \perp to the stratification). The coal samples were degassed prior to the experiments for about

70 hours, down to a vacuum of 0.013 Pa. Subsequently, to remove any traces of molecules entrapped in the coal micropores, helium was introduced into the system, and after 48 hours it was again degassed down to 10^{-3} Pa and to the constant resistance of the tensometers. The above mentioned gases were used as reference bases for the sorbates, because of their practical relevance to gas liberation in the technological and mining processes. Moreover, CO₂ and CH₄ differ considerably in their physio-chemical properties (Marecka 1999), which affects their sorptive capacity and the velocity of sorption processes in hard coals (Ceglarska-Stefańska 1993; Ceglarska-Stefańska, Zarębska 2001).



Fig. 1. Total volume of pores and volume distribution of pores of diameters 0.08—10 μ Rys. 1. Całkowita objętość porów oraz rozkład objętości porów w zakresie porów o średnicach 0,08—10 μ

The aim of this work was achieved by measurements of the sorption kinetics and of the variations of the outer coal dimensions in accordance with the following conditions:

- hard coal-CO₂ investigations were carried out under the following CO₂ pressure values: 7.07 hPa; 21.91 hPa; 29.08 hPa; 41.13 hPa; 68.16 hPa; 142.00 hPa; 399.91 hPa; 470.73 hPa; 519.95 hPa. The time of contact of the samples with the sorbate equalled 180 h, for each sorbate pressure value;
- hard coal-CH₄ investigations were carried out under the following CH₄ pressure values: 7.78 hPa; 21.72 hPa; 38.08 hPa; 72.66 hPa; 145.20 hPa; 197.12 hPa; 263.60 hPa; 341.44 hPa; 405.20 hPa; 482.58 hPa; 541.36 hPa. The time of contacting the samples with the sorbate was about 300 h;



Fig. 2. Total volume of pores and distribution of pores of diameters of 0.08—100 μ
Rys. 2. Całkowita objętość porów oraz rozkład objętości porów w zakresie porów o średnicach 0,08—100 μ

hard coal-CO₂ presorption-CH₄ sorption, investigations were carried out under CO₂ pressure values of: 4.11 hPa; 22.74 hPa; 47.91 hPa; 70.32 hPa; 132.05 hPa; 261.73 hPa; 394.62 hPa; 529.34 hPa; 532.95 hPa. Having reached the sorption equilibrium and under the highest applied CO₂ pressure, CH₄ was introduced into the system, under increments of pressure, at which stages measurements were taken. The subsequent total gas pressure values were; 599.04 hPa; 661.84 hPa; 771.68 hPa. The time of contact of the samples with the sorbate was equal to about 450 h. In calculating the sorption isotherm for this system the Markham-Benton equation was used (Spitzer 1981).

As a means of verification and as a source of potentially useful material, additional determinations of the real and apparent coal density were carried out, thereby aiding the definition of the coal's porous structure. The pycknometric elements used in these studies were helium and mercury (He and Hg). Additionally, on the other hand, automatic porosimeters: Pascal 440 and Pascal 140 CE Instruments, were used for the sample vacuum degassing and automatic filling of the dilatometer with mercury. They worked within a range of 0.1 to 400 MPa, which corresponds to the range of pore radii varying from 1900 to 58 000 nm. The results of the porosimetric studies gave information about the volume and pore surface area distribution within the range of macropores and partly, mesopores. The authors are aware of the limitations in the use of this type of measurement for hard coal samples (compressibility, various conformations of pores, which differed from those used in the derivation of the formula r = f(p) and the presence of closed pores in hard coal samples (Ciembroniewicz, Marecka 1990).

It is also commonly known that the results of the porosimetric studies do not take into account the pores of radii smaller than 5 nm. Moreover, the volume of mesopores is very small in hard coal samples. This is confirmed by the results presented in Figs. 1 and 2, and in Table 3, for instance, the lack of a plateau on the curve showing the total volume of pores indicates the presence of pores of lower diameters (d < 3.6 nm). They remain beyond the measuring range of the apparatus used.

TABLE 3

The results of the porosimetric and densitometric studies

TABLICA 3

d _{He}	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	V _p	$V_{\rm max} \cdot 10^{-2}$	$V_{\rm max} \cdot 10^{-2}$	² [cm ³ /g]
[g/cm ³]		[cm ³ /g]	the rang	e [nm]	
1.3445	1.2330	0.067	45.17	25–100	140.44
				100-2500	118.77
				2500-7500	110.79

Wyniki badań densymetrycznych i porozymetrycznych

3. Results and discussion

The results of the sorption and dilatation studies have been presented in the form of the relevant sorption-kinetic curves — Figs. 3–9, dilatation kinetics — Figs. 13, as well as the sorption isotherms — Figs. 10–12.

On the right side of the figures the values of the gas pressure, under which the kinetics of sorption or dilatation were studied, are given.

The investigations of the kinetics of sorption and diffusion of gases give the possibility to estimate the accessibility of the coal structure to the sorbate molecules. One should, however, remember that the possible deformations of the kinetic curve may be caused by inhomogeneity of the coal grains and of the pore-size distribution (Jungten et al. 1981). These relationships are clearly illustrated on the results of the CO_2 sorption kinetic studies on the coal sample investigated (Figs. 3, 4). The development of the area of the coal matter during grinding causes about a threefold increase of its sorptive capacity (within the whole range of the studied sorbate pressure values). Such effects were not observed in the system consisting of the hard coal and methane (Figs. 5, 6).

The important finding resulting from the analysis of the experimental data presented above is the recorded observation of the considerable increase of CO_2 sorption velocity with the increase of the sorbate pressure, which has not been observed for CH_4 kinetic sorption curves. For instance, for the highest pressure values used in the experiment (519.95 hPa for CO_2 and 541.36 hPa for CH_4), the time of reaching the apparent sorption equilibrium was 44 hours and about 217 hours, respectively. Moreover, the almost linear character of the CH_4 sorption kinetics on the coal sample in the form of a plate (Fig. 5) suggests that in this studied system the methane accumulation proceeds in the pores of greater diameters.

From the process of the sorption on the hard coal with CO_2 presorbed-CH₄ sorbed it appears that with the increasing total pressure of both sorbed gases a prolongation of the time needed to achieve equilibrium takes place. The introduction of methane into the system consisting of hard coal and carbon dioxide causes an insignificant increase of the sorptive capacity of the studied coal of grain size below 0.5 mm. (Fig.7). On the other hand, for two other forms of the samples, on the sorption kinetic curve for the mixture of gases $(CO_2 + CH_4)$, an increase of the sorbed amount of the sorbate may be observed (Figs. 8, 9). The analysis of the interactions between the coal and the mixture of gases needs account to be taken of the porous structure of the coal. It is known that the macropores play role of transporting pores, facilitating the penetration of gas molecules into the microporous structure of the coal by diffusion. This explains the difference in the pattern of the sorption process for the mixture of gases (CO_2 and CH_4), in dependence upon the sample grain distribution (Figs. 8, 9). The pores of the solid matter determine not only the active surface area of the sorbent under the designed experimental conditions, but also the transport of various substances. In the case of the pore openings of the order of magnitude comparable with that of the sorbed molecules, the possibility of selective sorption is determined by the difference in diffusion of the molecules through the "narrowings" (necks) of the pores — the smaller molecules sorb







Fig. 4. Curves of the CO₂ sorption kinetics, grains of $\phi < 0.5$ mm Rys. 4. Krzywe kinetyk sorpcji CO₂, ziarno ϕ poniżej 0.5 mm







Fig. 6. Curves of the CH_4 sorption kinetics, grains of $\phi < 0.5$ mm Rys. 6. Krzywe kinetyk sorpcji CH_4 , ziarno ϕ poniżej 0.5 mm



Fig. 7. Curves of the CO₂ presorption kinetics, and CH₄ sorption kinetics, grains φ < 0.5 mm
Rys. 7. Krzywe kinetyk presorpcji CO₂ i sorpcji CH₄, ziarno φ poniżej 0.5 mm



Fig. 8. Curves of the CO₂ presorption kinetics, and CH₄ sorption kinetics, grains $\phi = 1-1.5$ mm Rys. 8. Krzywe kinetyk presorpcji CO₂ i sorpcji CH₄, ziarno $\phi 1-1.5$ mm



Fig. 9. Curves of the CO_2 presorption kinetics, and CH_4 sorption kinetics, plate

Rys. 9. Krzywe kinetyk presorpcji CO2 i sorpcji CH4, płytka

earlier than the greater ones (the mechanism of kinetic separation) (Weishauptowa, Medek 1998). In the case of the studied coal these pore "narrowings" are most probably the result of the presence of numerous polar groups and non-reactive oxygen in the structure of the organic substance (Table 1).

The maximum sorption values obtained from the kinetic studies, close to the equilibrium, were used to draw the sorption isotherms a = f(p), presented in Figs. 10 to 12. The course of the sorption isotherms indicates for some effect of coal grain size on its sorption capacity. It may be seen that:

- for the hard coal-CO₂ system (Fig. 10) the sorption capacity values were obtained from both grain fractions, but too small surface area gives low *a* values for the coal in the form of a plate;
- for the system hard coal-CH₄ the effects observed are less pronounced than for the system: hard coal-CO₂. The low values of a indicate the insignificant sorptive capacity of the coal samples studied towards this sorbate. The minimum increase of a may be observed only for the sorbate pressure values above 350 hPa. It may be assumed that in this pressure range methane molecules are located in transport pores;
- for the system hard coal-CO₂ presorption-CH₄ sorption, only for the fraction of ϕ below 0.5 mm, on the sorption isotherm, no increase in sorption capacity of the samples was observed on the sorption isotherms. A significant increase, particularly under the highest experimental pressure used (771.68 hPa) is visible















Fig. 12. CO_2 sorption isotherm (up to 532.85 hPa) and of the mixture of CO_2 and CH_4 , at total pressure 599–771.7 hPa

Rys. 12. Izotermy sorpcji CO₂ (do ciśnienia 532,85 hPa) i mieszaniny CO₂ + CH₄ przy sumarycznych ciśnieniach: 599–771,7 hPa

for two remaining forms of the coal samples studied. The higher values observed for these samples may be also caused by locating both sorbates (CO_2 and CH_4) in "empty spaces" in the morphological cells of the parts of the studied coal and in the mineral substance. Therefore it is closely related to the inhomogeneity of the studied coal samples.

Summing up, the process of sorption of the small molecule substance in the hard coal proceeds as a penetration of the sorbate molecules in the elastic part of the carbon copolymer, overcoming cohesion forces (absorption), and on location of the sorbate in submicropores, using adhesion forces (adsorption) (Wójcik 1999). From the studies it presented appears that in a system consisting of hard coal and carbon dioxide the whole spectrum of adsorptive and absorptive phenomena is revealed. The further conclusion is that CO_2 is absorbed to a much higher extent than CH_4 . The above conclusions are confirmed also by the results of the dilatometric studies, carried out simultaneously with the sorption experiments. The change of outer dimensions of the coal sample in the form of a plate was traced parallely bot in parallel with and perpendicularly to the stratification.

The kinetics of dilatation indicates that the variations of the outer dimensions accompanying the process of CO_2 sorption are effectively higher for by one order of magnitude than in the case of CH_4 sorption. The coal dilatation accompanying the CO_2

sorption, under the maximum pressure of this gas is of the order of 0.1%. It may be assumed that during the CH₄ sorption (in the range of low pressures of this gas) in the system; hard coal-CH₄ — the location of methane molecules does not cause any changes in the outer dimensions of the sorbent, irrespective of the direction of the stratification. Therefore, in the range of methane pressure values investigated, the sub-micropore structure of the coal is not available to the molecules of this sorbate. In the system: hard coal-methane, location of the molecules of the sorbate takes place only due to the adhesion forces.

A very interesting course of the dilatation kinetics may be observed for the system: hard coal-CO₂ presorbed; -CH₄ sorbed (Fig. 13). Let us recollect that the introduction of methane into a system consisting of hard coal and carbon dioxide causes some reduction of the partial pressure of carbon dioxide in the sorptive space. The reduction of CO₂ pressure, the gas causing variation in the outer dimensions of the coal causes that coal is contracted resulting in coal contraction. The higher methane the pressure and the pressure of the gas reducing CO₂ concentration in the coal structure, the greater contraction of the sample. To illustrate this effect more clearly, in Fig. 13 the course of the dilatation of the studied coal during CO₂ sorption was presented only under the highest pressure applied (the points denoted with symbol x). Continuous lines denote the contraction of the samples, corresponding to reduction of their outer dimensions. Exclusively, in the case of the highest applied CH₄ pressure and prolonged exposure



Fig. 13. Kinetics of the variations in the outer dimensions of the coal when subjected to CO_2 presorption and CH_4 sorption

Rys. 13. Kinetyki zmian wymiarów zewnętrznych węgla,pod wpływem presorpcji CO2 i sorpcji CH4

time, the recovery of the sample outer dimensions to the value observed under the maximum applied CO_2 pressure was observed. This regularity is particularly well visible shown in the measurements of the variations in the outer dimensions (ε_{\perp}) in the direction perpendicular to the stratification. Such a clear relationship between the changes in outer dimensions of the coal and the composition of the gas mixture in the sorption space confirms the preferential adsorptive-absorptive interactions of the CO₂ molecules with the coal's organic substance.

The achievement of the states close to the equilibrium of the outer dimensions of the samples (after more than 250 h), in a system consisting of hard coal and a mixture of CO_2 and CH_4 , close to the maximum values of the dilatation (ϵ) for a system consisting of the hard coal and CO_2 explains why no disturbances on the sorption isotherms in the system: hard coal- CO_2 , presorption- CH_4 sorption were bserved.

Conclusions

The results of the petrographic and X-ray investigations, showing for numerous fissures in the structure of the coal studied, for a significant content of mineral matter and fusinite determine its (low) sorptive capacity.

From the course of the sorption kinetics for the system consisting of hard coal and single gases, CO_2 or CH_4 , it would appear to be demonstrated that with increasing sorbate pressure the time needed to achieve the sorption equilibrium is shortened, particularly in a system containing CO_2 .

The interaction in a system consisting of hard coal and methane proceeds mainly by physical adsorption, which is confirmed by the lack of variations in the outer dimensions of coal samples in the form of a plate.

For the system consisting of the hard coal- CO_2 the close sorption capacity values were obtained for both grain fractions. Too low surface area leads to low values of **a** for the coal in the form of a plate. Such clear effects have not been observed for the system consisting of hard coal and methane. Therefore it may be assumed that the system of sorptive pores in the studied coal is not accessible for a spherical methane molecule. Another words, the denso-metric parameters, related to the development of the molecular pores, determine the effectiveness of the gas storage.

The course of the sorption isotherms (above 600 hPa) in the system consisting of the hard coal-CO₂ presorption-CH₄ sorption indicates the effect of the grain size distribution of the studied material on its sorptive capacity.

The contraction of the samples, empirically found following the introduction of methane into a system consisting of the hard coal and pre-sorbed carbon dioxide may cause, even in the range of low pressures of both gases, the appearance of significant stresses in the rock mass and changes of its permeability.

It seems that two last conclusions are particularly important for mine exploitation. The analysis of the empirical data presented in this paper as well as in the work (Ceglarska-Stefańska, Zarębska 2001) confirms the effect of the structure of the coal pores on the diffusion rate of CO_2 and CH_4 and on their sorption capacity, on one hand. On the other one, it makes it possible observation of to see the relationship between the porous structure of the coal and its quality (i,e, the degree of metamorphism).

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