

The kinetics of sorption of a CO₂ and CH₄ mixture on hard coals due to the selective sorption of carbon dioxide

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The influence of the physical and chemical properties and the composition of the sorbed gas on the sorption capacity of hard coal must be taken into account in an analysis of such coals as specific collectors of mine gases. It follows from studies of CO₂ and CH₄ sorption on hard coals that the sorption process for CH₄ is slower than for CO₂. On the basis of analysis of sorption kinetics for these gases it might be assumed that when gases flowing through the bed are mixed, as a rule the gas flowing out from the bed is enriched with CH₄. The analysis presented was based on a comparison of the results of sorption studies of single gases (CO₂ and CH₄) and their mixtures in two hard coals (81.1% C and 90.12% C). Knowledge of these effects should facilitate further investigation of the relationship between the properties of a hard coal and methane evolution to establish those factors that enhance the rate and effectiveness of the process.

1. INTRODUCTION

The chemical and physical properties of hard coals are of great importance, due to the presence of methane gas in coal deposits, methane desorption and the dangers resulting from the process, as well as to the ecological problems created by hard-coal mining. In recent years, in the literature on natural gas-fuel resources a distinct emphasis on the development of projects and research activities oriented towards the extraction of gaseous fuels from the hard coal deposits is discernible, the latter being either unexploited state or those containing gases in subsoil storage, for instance, in cavings (post-mining subsidences). The subject is directly related to the permeability of rock, so the

determination of porosity structure of hard coals is one of the pre-conditions when forecasting their sorption properties [1-5]. Hard coal is a substance with an inhomogeneous capillary structure with pores ranging in size from molecular dimensions up to discernable macroscopic cracks. From a practical point of view the problem of the kinetics of sorption and gas diffusion in hard coals is linked to such problems as the transport of gases through a coal deposit, the location of the gas molecules in vapour form on the surfaces or in the bulk coal-mass [6-8]. Thus it is related to the way the gas storage in the deposits occurs as well as to the competitive sorption of the gases contained in the mine gas mixtures [9, 10].

A precise description of sorption dynamics in such a body as complex as hard coal is a very difficult task. At the same time as the process being studied occur such phenomena as the diffusion resulting from the transport of the molecules through the large macro- and mesopores as well as a significantly slowing in the movement of the sorbate through the mesopores due to the periodic adhesion of the molecules to the coal surface. The other form of diffusion is the very diffusion occurring in the elastic phase, which is similar to that occurring in polymers. Those two phenomena are described in the literature as so-called dual diffusion, which has been considered earlier by the analysis of diffusional transport in polymers [4]. The co-existence of diffusion and the sorption phenomena has been considered in the literature, among others, by [11-13]. Some authors state that the rate of the diffusion through the elastic phase may be higher than through a micro porous structure [14, 15].

Owing to specific physicochemical properties of hard coals, mass transport in hard coal involves several processes: normal and molecular diffusion, and diffusion activated in very narrow pores and in the elastic phase exclusively. On account of the fact that a comprehensive description of hard coals is not available and that sorption in hard coals is a most complex process (involving volumetric – surface-related aspects), no adequate, generally accepted quantitative description of diffusion processes is presently available. Moreover, most tests are run on cube-shaped specimens, that is why the well-known equations governing the diffusion processes are not applicable (for instance the grain radius cannot be determined). Apparently the parameter D_e/R^2 can be estimated from Timofiejev's equation, where R denotes the radius of an equivalent, spherical diffusion space/region containing only the largest pores that limit the rate of diffusion processes [16]. The effective diffusion-coefficient for hard coals is obtained on the basis of all involved mechanisms. Besides, hard coals are not sorbents with a rigid structure (such as activated carbons), which means that their external dimensions may vary during the sorption process (which is why the term "sorbent" is used throughout the text). Therefore, the comparison of test results obtained for active carbons and hard coals is not valid.

It should also be noted that the literature on the subject of sorption of gas mixtures is rather sparse, since even in the course of a qualitative analysis we tend to ask the question how the presence of another sorbing substance should affect the kinetics of the sorption process [17,18, 19]. Experiments carried out on systems made of rigid-structure sorbents (such as hard coal) and gas mixtures are only reported in a few papers.

Thus, on one hand, the processes of the gas transport are to be considered by accounting for the complicated structure of the coal sorbates and a possible overlapping of different phenomena within pores of different size, while on the other hand the selective sorption for individual components (CO_2 or CH_4) of the gaseous mixtures on the hard coals must also be considered.

2. EXPERIMENTAL PROCEDURE

2.1. Measuring apparatus and methodology

The sorption analysis for the hard coal-gas system was performed by the volume method [5,10]. The experiment procedure is as follows: The gas in the gas reservoir decompresses, pressure measurements are taken in the calibrated dosing volume. Afterwards the valve opens and gas flows to the measurement ampoule where the sorbate makes contact with the sorbent; at the same time the system registering pressure variations in the ampoule is activated. After valve is closed and the pressure in the dosing section is measured again, gas pressure variations due to the sorption in the ampoule can be monitored. To ensure the required accuracy of measurements, a volumetric pressure gauge type MKS BARATRON 722A is used. It allows pressure measurements over the range 0-4.0 MPa with an accuracy of ± 0.001 MPa. At the same time an incorporated pressure sensor indicates pressure variations in milliseconds, and that allows for the reliable registration of this parameter. Iteration of this procedure at various gas pressures yields a succession of points on the isotherms for the sorption process. When a near-equilibrium condition is established, at the last predetermined sorption pressure the desorption process takes place when the gas pressure in the ampoule is gradually decreased. The valve releases the gas from the apparatus for the purpose of sampling, to be used in chromatographic analysis. The full apparatus is thermo-static and measurements can be taken at a constant temperature (298 K).

Variability of physicochemical properties that affect the sorption process in coal makes the interpretation of results an extremely difficult task. To overcome the potential problems the measuring ampoule contained several coal plates with the total mass about 30g, so the calculated values of sorption capacity of tested coals are all averaged. The measurements were performed for the coal plates of a 0.015 x 0.015 x 0.005 m size cut from a cob of the original coal to obtain an

intersection face parallel or vertical to the bedding of the coal. It should be noted that the kinetic measurements for the hard coal/gas systems require prolonged pumping operations to reach a quasi-equilibrium state so about 200 hrs were necessary to obtain a single measurement point [20].

The near-equilibrium condition was assumed when the registered pressure variations in the ampoule fell in the range ± 0.002 MPa. The advantages offered by the volumetric method are: stabilisation and monitoring of the measuring system temperature is possible; measurements of sorption kinetics can be taken regardless of the speed of this process. However, in order to obtain reliable results it is necessary that coal samples be specially prepared: previously absorbed gases and vapours, particularly from the micro-pores, must be removed from the coal surfaces. To achieve this, coal samples to be used in the apparatus, prior to measurements, were subjected to a long-lasting process of gas removal, until the vacuum of an order of 10^{-3} was established and strain gauge resistance became constant. The efficiency of gas removal was further improved by repeated "rinsing" of the samples in helium. Also, helium was employed to calibrate the dead zones in the ampoules containing the coal samples. Helium used in calibration remained in the measuring section for about 24 hours. Rao observed that helium may fill the pores in coal structure whose initial (entrance) dimensions exceed 0.5 nm [21]. Atoms of helium are not adsorbed and provide kinetic energy to molecules of adsorbed vapours and gases, displacing them from the hard coal surface, hence the dead volume obtained from calibration with the use of helium takes into account the micro-pore volume. The amount of the individual absorbed gas (a) was computed from the material balance of the dosed gas and the non-absorbed one by use of the gas laws according to the Beatty-Bridgeman relationship while for the gas mixture the sorption kinetics were determined by using the Langmuir isotherm extrapolated by Markham and Benton for two-component gas mixtures [9].

2.2. Porosity measurements

Porosity measurements were taken with the use of an automatic porosimeter; Pascal 440 CE Instruments and Pascal 140 operating in the pressure range 0.1-400 MPa. The sample was evacuated to achieve a vacuum of 0.1 kPa, then the dilatometer was automatically filled with mercury. Thus we obtain pore volume and surface distributions in the range of macro- and meso-pores, the corresponding radius range being 1900-58000 nm. It is readily apparent (see Fig 1) that the total volume of pores over the measured range is larger than the coal sample B. In the interpretation of results we considered all reservations and doubts that arose in connection with applicability of such measurements to the analysis of hard coal structure: assumed a cylindrical shape of pores, the effects

of elevated pressure on deformation and possible damage to macro-structure and the possible opening of previously closed pores.

2.3. Sample material

The subject of the analysis were Polish hard coals originated from Górnośląskie Zagłębie Węglowe (upper Silesia): a low-carbon coal sampled from KWK Brzeszcze (V^{daf} 40,87 %; C^{dsf} 81,06 %) , bed 325, level 430 m (denoted in this paper as coal *B*) and the coal with a medium extent of metamorphism originated from KWK Moszczenica (V^{daf} 22.32 %; C^{dsf} 90.12%), bed 510 / 1-2 level 240 m (denoted in this paper as coal *M*). The characteristics of the coal material, in the form of petrographic and densitometric analysis have been presented in earlier papers [22, 23].

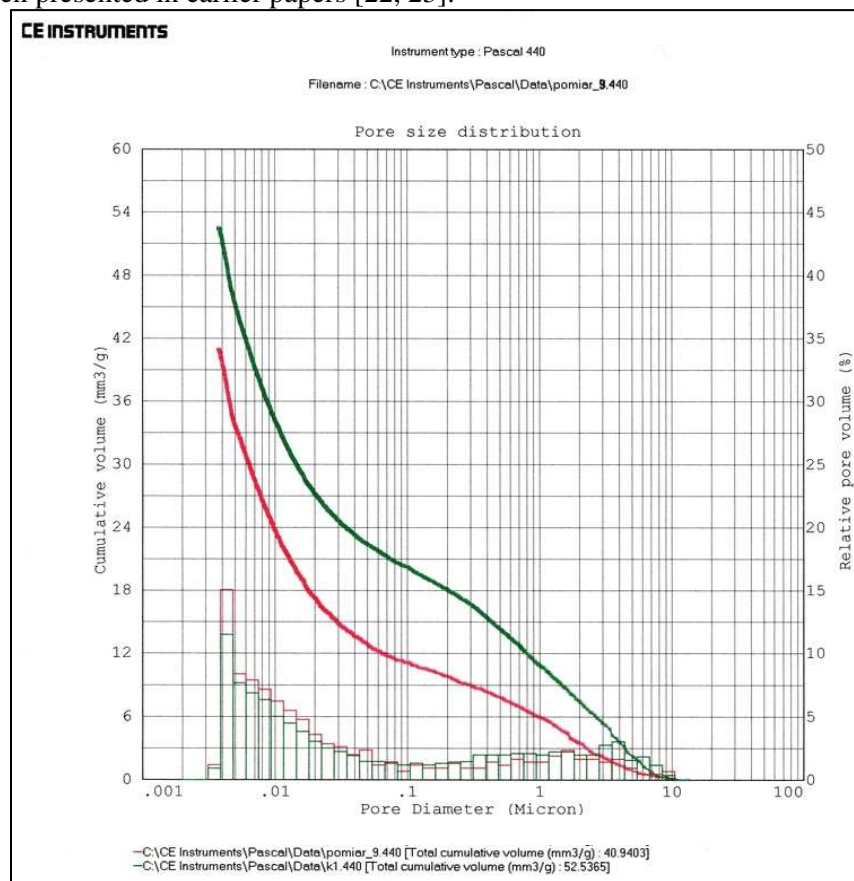


Fig 1. Results of porosity measurements taken with the use of a porosimeter Pascal 440 CE Instruments on coal M — and coal B —

Carbon dioxide and methane were used in this study as they both are crucial for the gas escape met initiated by deposit mining as well as there being numerous literature data on kinetic and static investigations related to various mining technologies. Moreover, those gases - as the main components of mine gases - from a physicochemical point of view, differ substantially from each other as to their chemical character, the kinetic diameter of their molecules and their structure, i.e., the factors which affect the course of any sorption process.

3. RESULTS AND DISCUSSION

The measurements of sorption for the same sorbates (carbon dioxide, methane or a composition of these two) were taken on two coal sorbents *B* and *M*, as the main objective of the experimental programme was to establish the relationship between the properties of hard coals (porous structure, metamorphism, sorption capacity, variations of external diameter in the course of gas sorption/desorption) and the process of methane release, and to find the major determinants of this process. Only selected results are provided in the present study. The effects of sorption of other gases (carbon dioxide) on methane desorption seem to be of primary importance. Investigations of high-pressure sorption of methane and carbon dioxide will surely help to highlight the mechanisms of gas deposition in coal beds and of rock and gas outbursts in mines [6, 18, 19]. There are major difficulties to be overcome: new experimental programmes have to be developed with a view to achieving adequate and reliable results applicable to the real conditions in mines. Also, correct interpretation of results is a key issue. Sorption of gas mixtures (made of two or three components) is a fundamental issue for coal mining activities. It is assumed that the greater proportion of gas in the coal bed is methane, deposited there as a result of various adsorption/ absorption processes.

The relationship between sorption and diffusion of CO₂ and CH₄ in hard coals and their petrography is well documented in the literature on the subject, that is why the investigation used several types of hard coal as sorbents in the experiments in preference to activated carbons. It will be realised that even a single series of experiments is a very time-consuming process, as the full measurement procedure for the sorbent/sorbate system lasts about three months: it takes quite a long time before the sorption equilibrium is established in hard coals; particularly when samples are in the form of thin plates.

As was mentioned earlier, in the literature on the gas sorption on hard coals, there are considered not only the absorbing capacity of the hard coal substrate and the retention of the sorbate molecules in the coal structure but also measurement of the kinetics of sorption and diffusional processes are of

importance, as such investigations provide extra information on the porosity of the sorbents in question and the gas transport mechanisms [10, 12, 13, 20].

The most frequently-applied analytical method is the kinetic plot presenting the rate of sorption as a function of time. The process is characterised by the asymptotic value of the amount of the sorbate at given conditions of temperature and pressure (T, p). A kinetic study provides a time dependence of the sorption rate as well as it determines the factors that affect the overall kinetics, i.e., sorbent and sorbate character as well as the course of the process. The sorption rate measured as the increase of the sorbate's mass per a time unit is decreasing whilst the other experimental parameters are held at a constant level. Due to the fact that for sorption processes, long time-spans are needed to reach equilibrium of the sorption, the results obtained by these authors are presented in this paper in the form of diagrams with two time scales for the coal-sorbate contact: 7h and 100h.

As to the individual gases (CO_2 or CH_4) the experimental data on the sorption kinetics have been reported in our previous papers [22, 23]. They indicated that - within the region of the sorbate pressures from 0 to 4.0 MPa - the sorption capacity of both coals is approximately two times higher for methane as compared to carbon dioxide. The results agree with those of other authors [24]. The difference found between methane and carbon dioxide are due firstly to their different physicochemical properties while on the other hand they depend on the carbon content (%C) and the porosity of the coal samples. The sorption analysis carried out using various sorbates and under various conditions such as temperature, pressure or the extent of disintegration of the samples confirms a hypothesis that hard coals are diporous sorbents with a developed system of sub-micropores, a significant fraction of which have diameters comparable to the sizes of the sorbate molecules [8, 14, 15, 25, 26]. Another type of the pores are macropores, which were found by porosimetric study, however according to the relative number of macropores in hard coals is low [17]. The macropores are the fastest routes for transport of the sorbate within the internal structure of the coal. The accessibility of sub- or micropores for different sorbates depends not only on the type of the coal but also on the dimensions of the sorbate molecules, their shape and the sorbates' critical temperatures. It is highly reasonable to assume that - by the temperature and pressure conditions applied in the experiments performed - carbon dioxide occurs in a vapour state while the methane represents gaseous substrates as at temperatures higher than the critical one any condensation of the methane in the pores is highly unlikely, bearing in mind that the density of the adsorption phase ought to be lower than the density of a liquid at the boiling temperature by the normal pressure. The above preconditions result in a more rapid achievement of sorption equilibrium for the CO_2 - coal system when compared to the CH_4 - coal one, regardless of the way the

individual gases are dosed into the phial. The papers published so far [22, 23], which analysed the interactions between hard coals and low-molecule substances lead to the conclusion that the hard coals of a different extent of metamorphism are selective in character.

In order to support that idea the three following systems were studied:

- coal - mixture of CO₂ + CH₄ (41.5% CO₂ and 58.5% CH₄)
- coal - presorption of CH₄ - sorption of CO₂
- coal - presorption of CO₂ - sorption of CH₄

- **coal - mixture of CO₂ + CH₄ (41.5% CO₂ and 58.5% CH₄)**

The experimental data presented in Figures 2 and 3 show that after one hour's duration time of contact of the sample with the sorbate on the plots of the changes of the relative sorption (a_t/a_{max}) a distinct inflection for the lowest imposed pressures appears. That course may mean that the extent of achievement of sorption equilibrium depends on the sorbate's ability to overcome the energy barrier due to the diffusion through the narrowed ultra-micropores. This conclusion also appears to have been reached by Saunders [18] and Rao [20].

Analysis of the plots indicates that the sorption of the gas mixture on the coal *B* (Fig. 3) is substantially faster than the one on the coal *M*. As the same composition sorbate was used for the both cases the fact may be linked to the different extent of metamorphism of the studied coals and their petrographic compositions.

It is worth remembering that coals of a higher extent of metamorphism, e.g., coal *M*, contain a low number of low-molecular links and a high number of macromolecules of a higher degree order [8] so the structure of these coals is more rigid than of those with a lower degree of carbonation, and is less susceptible to penetration by vapour or gas molecules. It reduces the accessibility of the sorbate molecules to the pores while the possibility of their separation results from the different diffusion rates for the molecules when going through the pores' contractions, i.e., the smaller molecules are being sorbed faster than the bigger ones to follow the separation mechanism due to the kinetic effect. The effects are the most pronounced at the lowest pressures when the sorption space is clean (degassed).

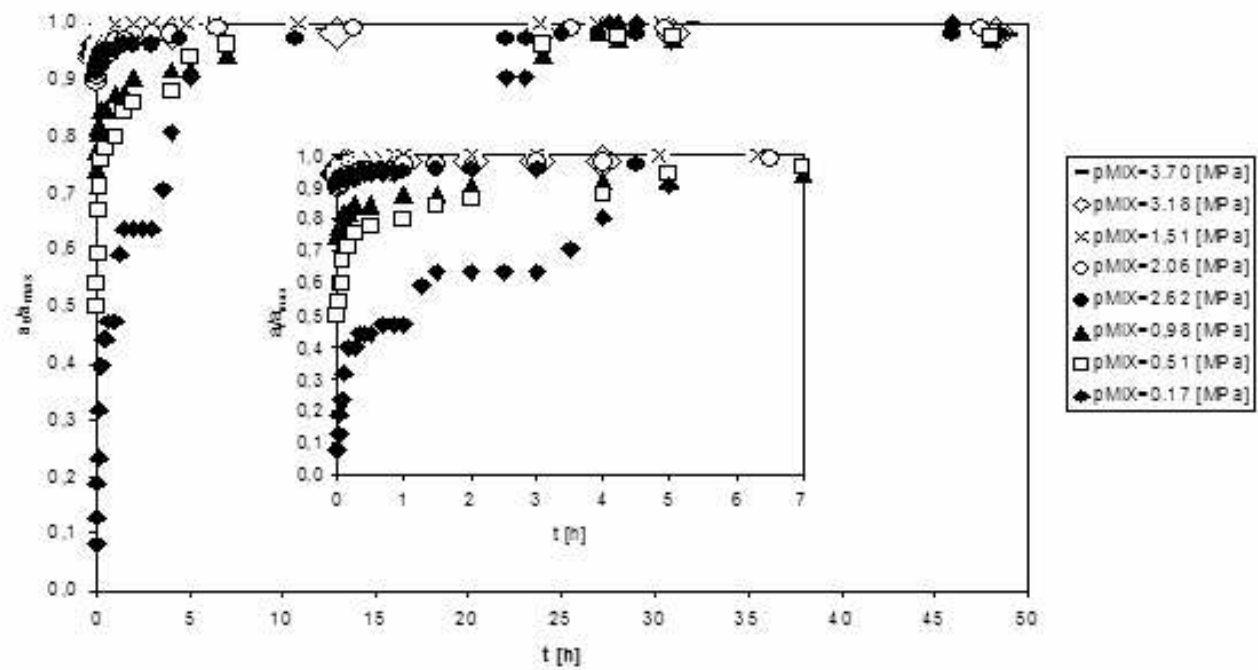


Fig. 2. Curves of the relative sorption a_t/a_{max} of coal M towards a $CO_2 + CH_4$ gas mixture.

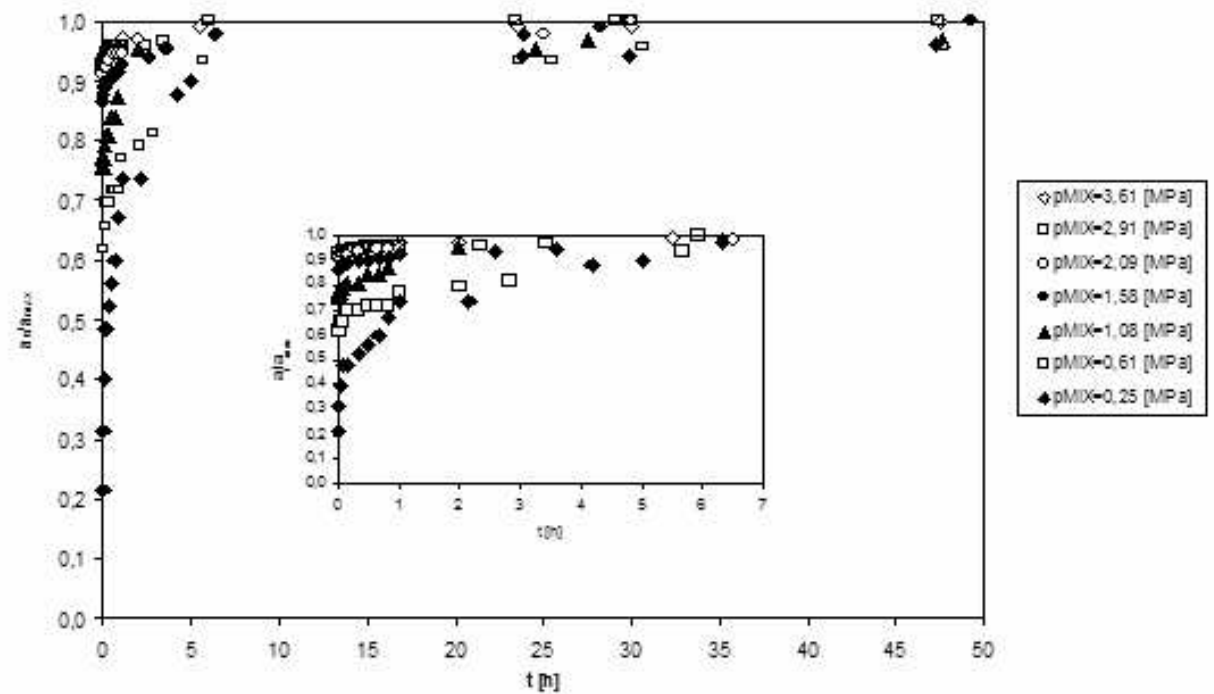


Fig. 3. Curves of the relative sorption a/a_{max} of coal *B* towards a CO₂ + CH₄ gas mixture.

- **coal - presorption of CH₄ - sorption of CO₂**

The experiment was performed starting with initial sorption of methane, then carbon dioxide was introduced to the measurement system at a gas pressure higher than 2.5 MPa. In order to distinguish those two sorption processes the former, i.e., the contact of the coal samples with the first dosed sorbate will be termed *presorption*. In the presorption curves for methane (Figs 4 and 5) there are evident long times $t_{0.5}$ particularly pronounced for the case of low-carbonated coal *B*. It is probably due to the blocking of the inlet openings to the pores by the spherical methane molecules. Therefore a longer time is needed for the diffusion of the gas within the coal matrix and for the achievement of sorption equilibrium. [6, 13, 19]

When another gas, i.e., carbon dioxide is introduced to the system of coal - CH₄, the considered system corresponds to a coal/gas mixture one. For such a system as well as for the all range of the applied pressures for the system coal - (CO₂+CH₄) mixture the sorption capacity was estimated by means of the formulae proposed by Markham and Benton [10].

When CO₂ is introduced to a coal-methane system, which is in a state of sorption equilibrium, a reduction of $t_{0.5}$ parameter is noted (Figs 4 and 5). It may be supposed inferred that such a shape of the kinetic curves results from an enhanced access to the coal structure for the smaller carbon dioxide molecules as the structure is extended at that moment by the previously absorbed methane molecules. The analogous easily discernable - as to the absolute values - course of the $a_t/a_{max} = f(t)$ curves after the introduction of CO₂ to the systems studied is worth noting. That kind of regularity of the relative curves is not observed for the relative sorptions for the next studied system, i.e., coal - presorption of CO₂ - sorption of CH₄

- **coal - presorption of CO₂ - sorption of CH₄**

The experiment was also run initially as the sorption of a single sorbate, i.e., carbon dioxide and it was considered as presorption of that gas, then the other sorbate, i.e., methane was introduced to the studied system. The results obtained are presented in Figures 6 and 7. Apparently, by the process of the sorption of carbon dioxide for both coals some regularity occurs, i.e., the time of achieving of sorption equilibrium is reduced by increasing CO₂ pressure. It is also worth noting that that time in every case studied was shorter for coal *M*.

The experimental data also indicates that the use of methane does not result in any significant changes of the sorption capacities of the coals.

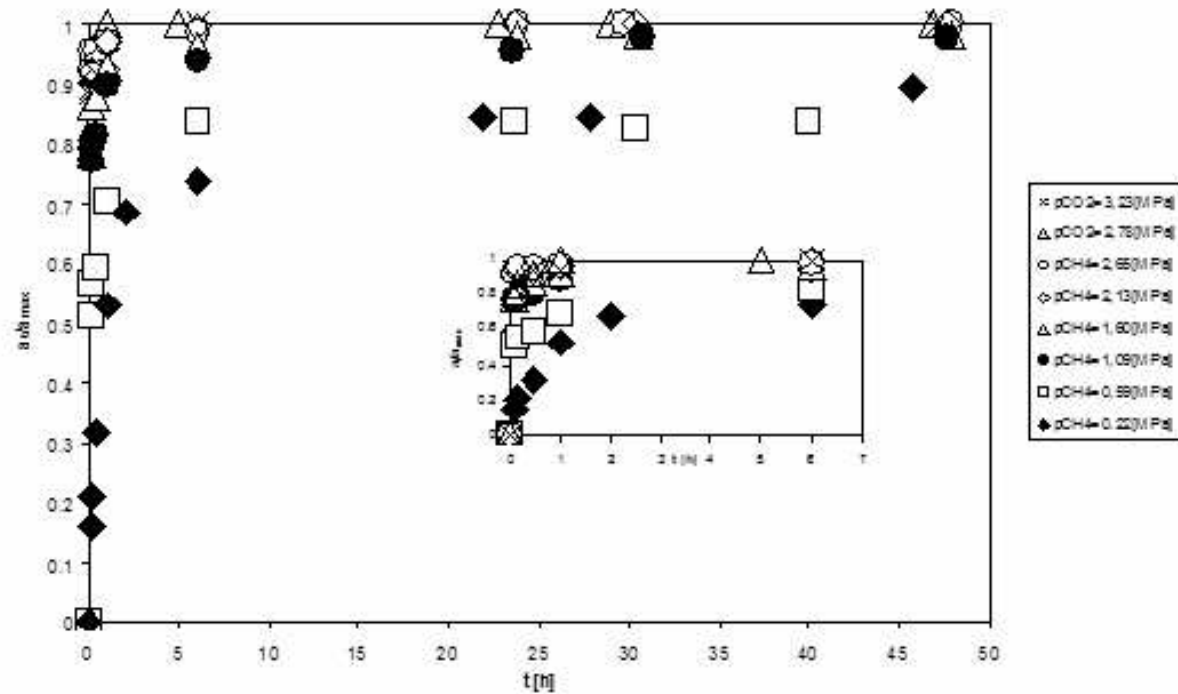


Fig. 4. Curves of the relative sorption a_t/a_{max} of coal *M* towards a CH₄ presorption and CO₂ sorption.

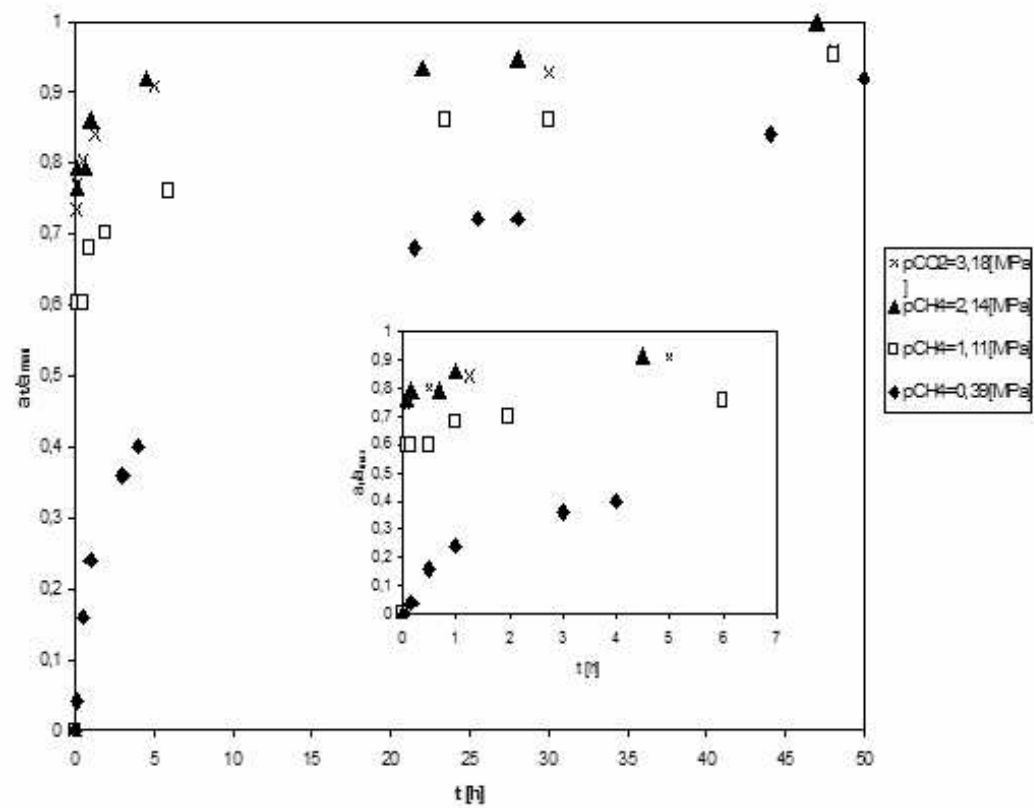


Fig. 5. Curves of the relative sorption a_t/a_{max} of coal *B* towards a CH_4 presorption and CO_2 sorption.

Thus, for instance, in the case of the coal *M* the methane introduced to the coal-carbon dioxide system only causes a relatively small increase of the sorption ability of the coal.

It seems reasonable to believe that the spherical methane molecules locate themselves only in the transport pores as the sorption space is already packed by the carbon dioxide molecules [2, 7].

4. CONCLUSIONS

As the experiments were conducted every time using the same gases and the gases were introduced to the studied system in the same order, it seems reasonable to believe that the crucial factor is the differentiated structures of the coals as it has been stated earlier. Those different physical and chemical structures are reflected in the selective character of the coal matter. The results obtained also indicate that the coals exhibit a sorption preference for carbon dioxide molecules. Moreover, when analysing the sorption results, particularly from the kinetic point of view, one has to consider the contribution of the macerate groups, hence the dependence of sorption and diffusion of CO₂ and CH₄ on the petrographic composition of the coals. Also the enrichment of the desorbed gas in the methane component relative to the initial mixture composition either for the low-carbonated or medium-carbonated coal confirms the preferential sorption of CO₂ from the binary mixture of CO₂ and CH₄ and this behaviour results from the structure and physicochemical properties of the sorbates.

The above-presented analysis has not only a theoretical character but could be applied to real coal mining conditions.

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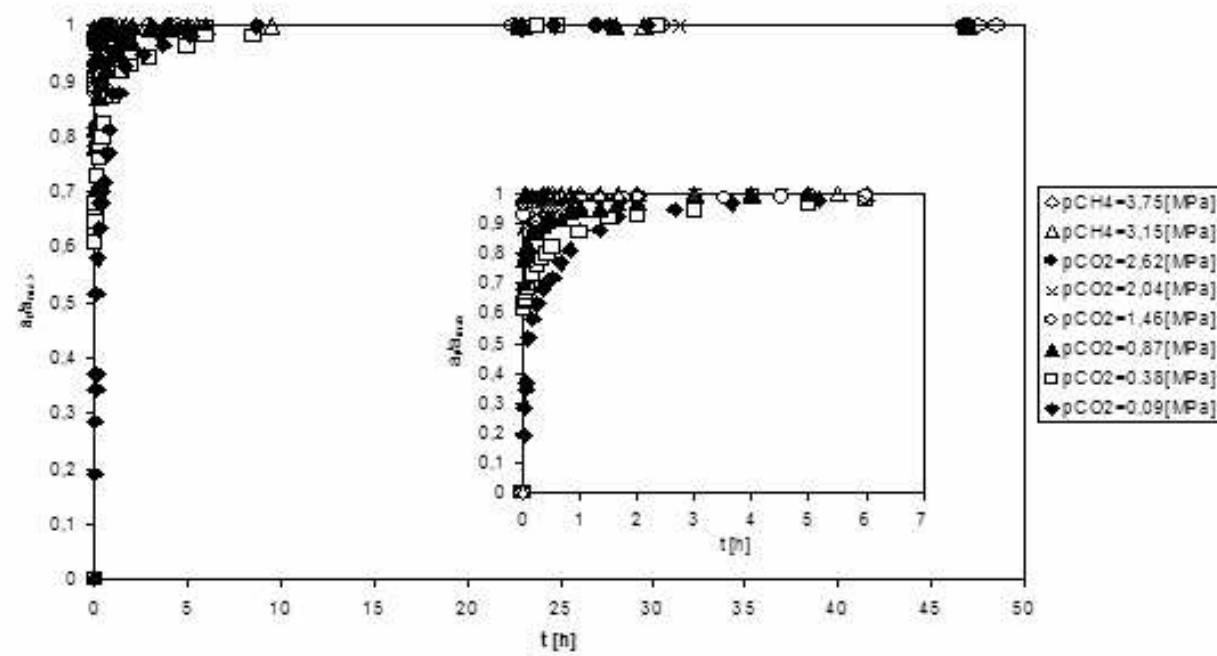


Fig. 6. Curves of the relative sorption a_t/a_{max} of coal M towards a CO_2 presorption and CH_4 sorption.

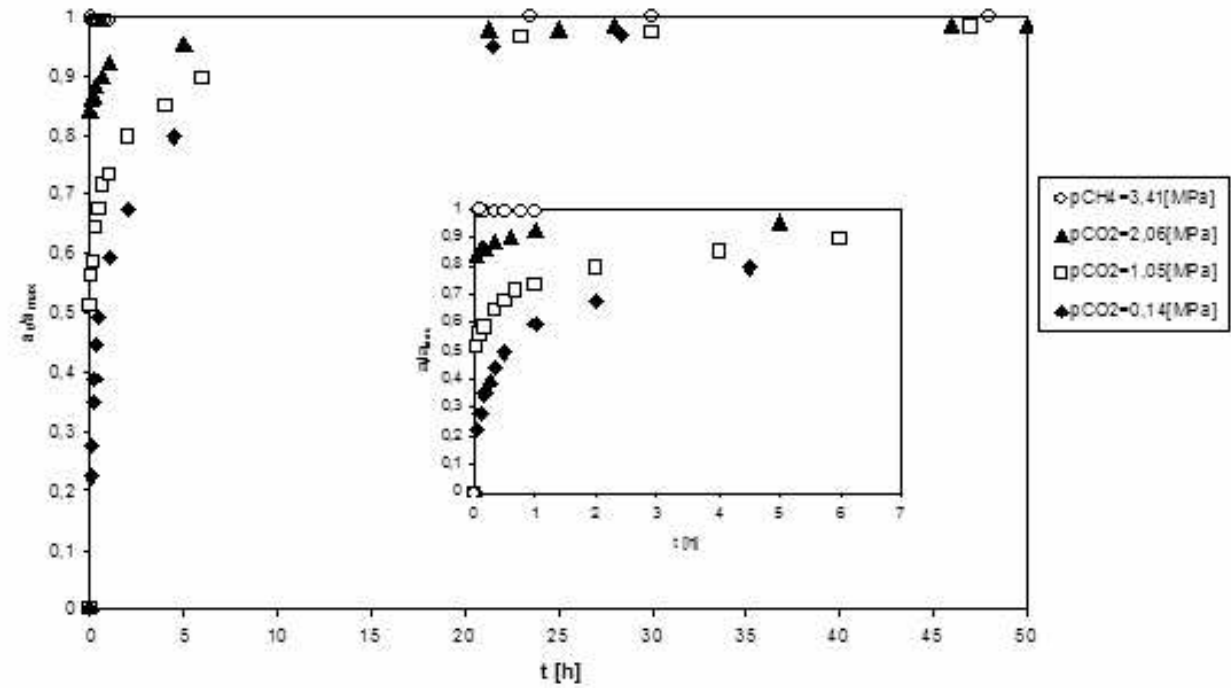


Fig. 7. Curves of the relative sorption a/a_{max} of coal *B* towards a CO₂ presorption and CH₄ sorption.

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