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PROGNOSTICATING FIRE HAZARDS IN GOAFS IN POLISH COLLIERIES***

1. INTRODUCTION

Hard coal has a strongly heterogeneous capillary structure, containing pores ranging from molecular sizes to fissures and cleats revealed macroscopically. That is why in practical applications the problem of gas sorption and diffusion kinetics is considered to involve such phenomena as gas migration through the coalbed, location of gaseous molecules in the form of vapour on the coal surface and in the bulk of coal (gas storage in coalbeds) and selective sorption of gases from mine gas mixtures [1, 16]. Comparison of several coal types presents a major difficulty and as their parameter may vary from one coal deposit to another and from one location to another within the same colliery. The description of sorption dynamics on such complex structures as coals is most difficult [6, 8, 10, 13, 17]. The process involves two concurrent diffusion processes: that associated with molecules being transported through large macro- and mezopores, and much slower displacement of the sorbate through micropores, associated with temporary retention of molecules on the surface, and the proper diffusion in the elastic phase, the process similar to that taking place in polymers. These phenomena are often referred to as the dual diffusion, considered in the analysis of diffusive properties of polymers [7]. In literature on the subject we find reports that have established the co-existence of diffusion and sorption phenomena and this issue is addressed in numerous publications. Some authors even suggest that the rate of diffusion through the elastic phase might be larger than through a microporous structure. To a large extent, the basic structure of hard coal, involving the aromatic cyclic, hydrogenated

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or aliphatic chain concentrations exhibits the polar behaviour. Defects and concentrations of condensed aromatic groups are polar to a certain extent, due to the presence of đ-electrones located in the benzene rings. Polarity of hard coals is mostly associated with the presence of reactive oxygen groups, partly nitrogen and sulphuric groups. Hydrophilic groups are responsible for the coal's tendency to spontaneous self-heating, its flotability, reactivity and swelling. Any change in reactivity of those groups is revealed in the value of the heat of wetting, particularly in the course of sorption processes. The concentration of oxygen polar groups can be determined by chemical analyses, by the IR spectrum analysis, by measurements of the heat of wetting or by sorption tests. Chemical processes involving hard coals occur mostly on the coal surface, passing through the stage of inter-phase processes. The coal surface contains numerous groups which act as regulators of the hydrophilic behaviour of the coal surface. These groups, particularly the oxygen groups, largely affect the process of sorption of polar substances and in a way control the sorption of apolar substances, such as methane or a series of chain or cyclic hydrocarbons [15].

Sorption of selected gases (ethane, ethylene, propane, propylene) on hard coals has to be considered during mining operations because of potential risk of coal self-heating, leading to endogenous fires, explosions and gas outbursts [2–5]. Research into hard coal--gas systems is fully merited to enable reliable forecasting of fires and explosions in mines, in the context of preventive measures to be put in place Despite major efforts to improve the safety features in mines, fires and gas outbursts in collieries are still fairly frequent. This state of affairs is attributable to the specificity of underground excavations whose volume is limited and where hazardous gas concentrations soon exceed the admissible levels. Mining operations open the migration paths for gases, generating the pressure difference and thus produced pressure gradient gives rise to the flow of free gases towards the lower pressure regions. The pressure gradient has its peak value in the direct vicinity of excavations and tends to decrease with the distance from the walls. The outflow of gases and water from the pores, cracks and fissures generates the pressure gradient between the macropores, cracks and micropores in coal. As a result, this process triggers the desorption of gases sorbed in coal, which in turn gives rise to the gas pressure gradient between the micropore walls and macropores, leading to convergence [11]. Cutting off certain parts of the rock strata from the ventilation network in the mines does not eliminate those phenomena because mining operations cause major cracks in the rock strata, forming connections between its various regions and thus produced strains and faults lead to gas migration to the subsurface regions. Mining hazards arise when gas is released from coal during the mining operations or when gases begin to interact with the exposed coal face or the coal being mined. Exposure of a fresh wall to air leads to an exothermal reaction between coal and oxygen, which may give rise to self-heating of coal. Reliable forecasting and control of mining hazards requires an accurate and early diagnosis of their major determinants. Exothermal oxidation processes taking place in the mine workings are accompanied by emissions of gases: carbon oxide, carbon dioxide, hydrogen and hydrocarbons. In the context of potential self-heating of coal, non-saturated hydrocarbons (ethylene, propylene) seem to play a major role. The release of those gases is responsible for reduced oxygen concentration in the area. It is worthwhile to investigate the influence of coal rank and porosity on the sorption process and to perform desorption tests as this process appears to be responsible for transfer of those bonds from hard coals to the mine atmosphere [9, 14]. Results of the projected research program will be utilised in reliable forecasting of mine hazards, thus improving the safety features in collieries.

2. METHODOLOGY

Tests consists mainly in sorption and desorption measurements of selected gases- mine air components, whose presence is evidenced by chromatography analyses. Sorption measurements are taken by the volumetric method, using a sorption meter Micrometrics ASAP 2010 (Accelerated Surface Area and Porosity Analyser) for investigating the structure and physico-chemical parameters of substances. Plots of the relationship between the amount of sorbed sorbate and its equilibrium pressure at constant temperature are referred to as sorption isotherms, giving us a good insight into the surface characteristic of the investigated material. Interpretation of sorption isotherms enables us to define the surface development condition, pore type, the scale and nature of the effective area. Hard coal samples from collieries in the southern and western Poland (Sz – Szczygłowice, BB – Bobrek, CW – Chwałowice, JW – Jaworzno) were collected in accordance with the procedure set forth in the standard PN-90/G-04502. Thus obtained coal samples were first ground to obtain the grain diameters 0.5–0.7 mm to average their physico-chemical properties. Prior to the tests, thus prepared samples were kept in the atmosphere of nitrogen, to reduce moisture absorption from the surroundings and to prevent oxidation of the coal surface.

Table 1

Characteristics of the coal samples investigated

Coal	A [%]	V^{daf} [%]	C^{daf} [%]	W^{a} [%]
SZ	3.48	33.93	83.82	1.76
BB	4.23	31.80	77.12	3.08
CW	2.65	35.62	79.29	3.39
JW	14.45	28.39	57.83	11.11

Explanations: A – ash content, V – volatile matter, C – carbon content, W – moisture content. Superscript: *daf* – dry and ashless state, *a* – analitycal state.

The elemental analysis of investigated coal samples was performed in the accredited laboratory of the Central Mining Institute in Katowice. Results are summarised in Table 1. It is found out that coal from the colliery JW has the lowest content of dry and ash-free carbon (57.83%) whereas coal from the colliery SZ has the highest carbon content (83.82%). The first stage in the measurement procedure involves the preparatory treatment of samples. Prior to the experiments, previously sorbed gas molecules and vapours of various chemical substances have to be removed from the coal's surface and from the pores. The coal samples are evacuated under vacuum, of the order of 10^{-3} Pa and subjected to the helium rinse for about 24 hours, under pressure of the order of several kilopascals. Helium atoms are not sorbed and their kinetic energy helps remove the adsorbed/absorbed gases from the coal surface [12]. Besides, helium is able to penetrate into the structure of porous substance, the pore size nearing 0.5 nm. This fact is of key importance because the results of pore size classification for hard coals of different ranks reveal major heterogeneity of architecture of their porous structures.

3. RESULTS AND DISCUSSION

Results of low-pressure tests of gas sorption (ethane, ethylene, propane, propylene) on selected hard coal samples are given in the form of sorption/desorption isotherms (Figs 1–16), showing the sorption capacity for investigated systems. Sorption capacity of tested hydrocarbons, particularly non-saturated ones, appears to be relatively low, which may be attributable to the adsorption mechanism involved.

Plotted graphs indicate that JW coal displays the highest sorption capacity with respect to the investigated sorbates (Figs 17–20). In the case of this coal, the maximal sorption capacity is registered for propylene and its value is five times higher than for remaining coals. Sorption capacity with respect to propane molecules is the highest, too. As regards this sorbate, the sorption capacity of JW coal is 23 times higher than in other coals. Sorption capacity for ethane is 10 times higher and for ethylene 5 times higher than the values registered for the highest rank coal with the lowest oxygen content, that is SZ coal (Tab. 1). The maximal sorption capacity of the investigated coal with respect to propane and propylene is attributable to the molecular sieve effect. The coal from the colliery JW has the highest porosity and at this stage that may suggest its specific sorption behaviour both on the surface and in the coal bulk. It is reasonable to suppose that its high sorption capacity is associated with easy accessibility of pores to molecules of the two sorbates. The predominant role of adsorption and gas transport processes is evidenced by desorption curves. In the case of JW coal, a two times higher gas desorption capacity is observed than for remaining coal samples. The fact that sorption of non-saturated hydrocarbons seems to be a favoured process can be attributable to interactions between π-electrons in dual bonds and polar groups on the coal's surface. It seems to corroborate the findings reported in literature on the subject, suggesting that adsorbate-absorbate interactions play a more important role than those between adsorbates and adsorbents. The basic structure of hard coal, involving the aromatic cyclic, hydrogenated or aliphatic chain concentrations exhibits the polar behaviour to a greta extent. Defects and concentrations of condensed aromatic groups are mostly polar in nature, due to the presence of π-electrones located in the benzene rings. Polarity of hard coals is largely determined by the presence of reactive oxygen groups, partly nitrogen and sulphuric groups. Hydrophilic groups are responsible for the coal's tendency to spontaneous ignition, flotability, reactivity and to swelling. Any change in reactivity of those groups is revealed in the value of the heat of wetting, particularly in the course of sorption processes. Chemical processes involving hard coals occur mostly on the surface, passing through the stage of inter-phase processes. The coal surface contains numerous groups which act as regulators of the hydrophilic behaviour of the coal surface. The presence of these groups, especially oxygen groups, largely affect the process of sorption of polar substances and control sorption of apolar substances, as evidenced by the obtained isotherms.

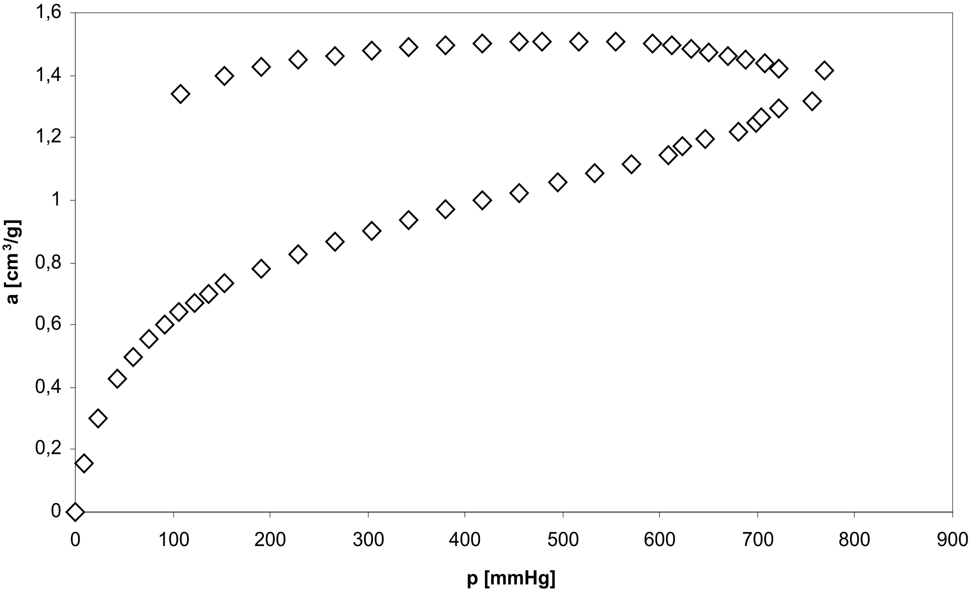

Fig. 1. Isotherms of propylene sorption/desorption on SZ coal

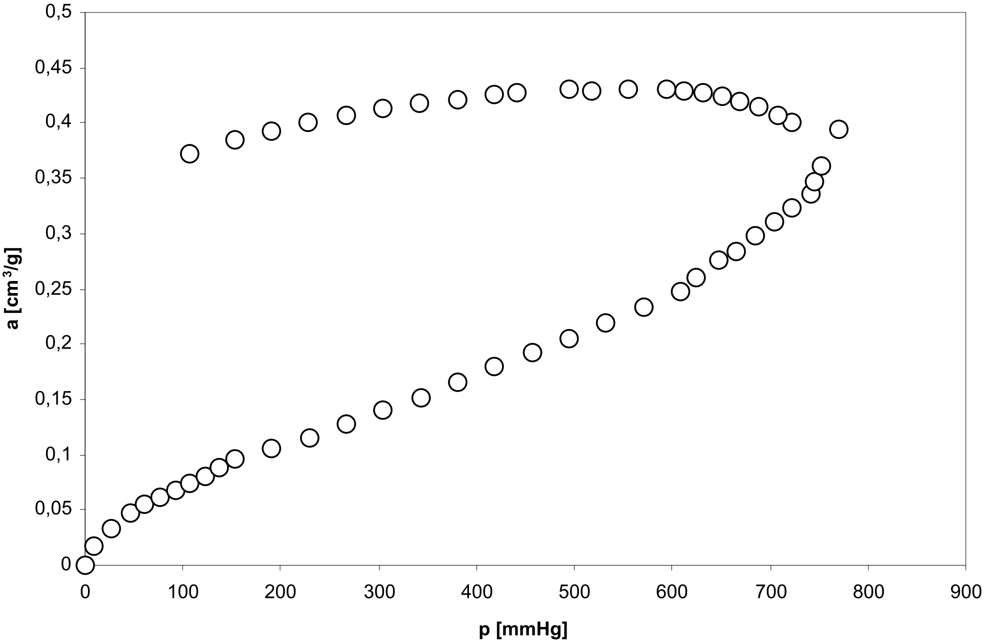

Fig. 2. Isotherms of propane sorption/desorption on SZ coal

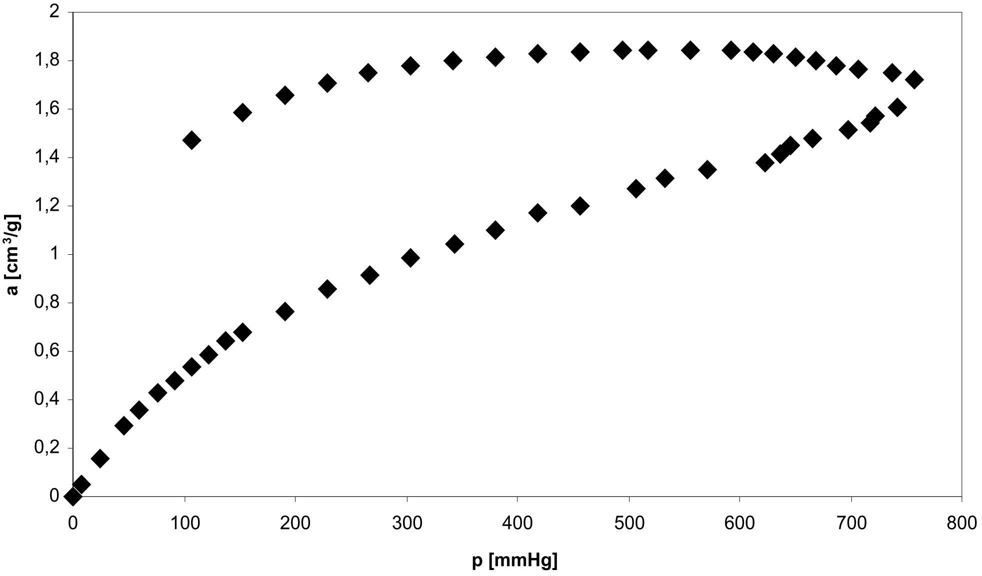

Fig. 3. Isotherms of ethylene sorption/desorption on SZ coal

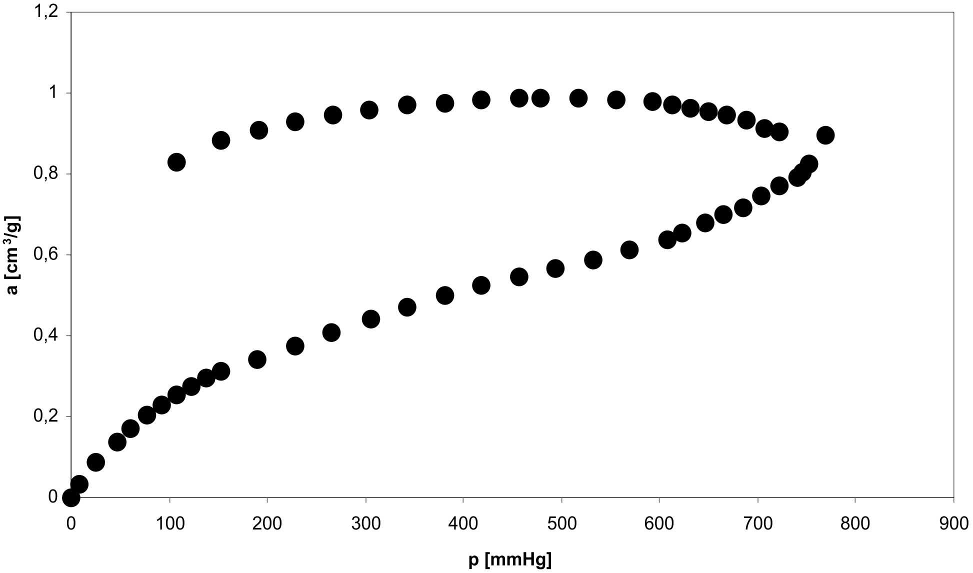

Fig. 4. Isotherms of ethane sorption/desorption on SZ coal

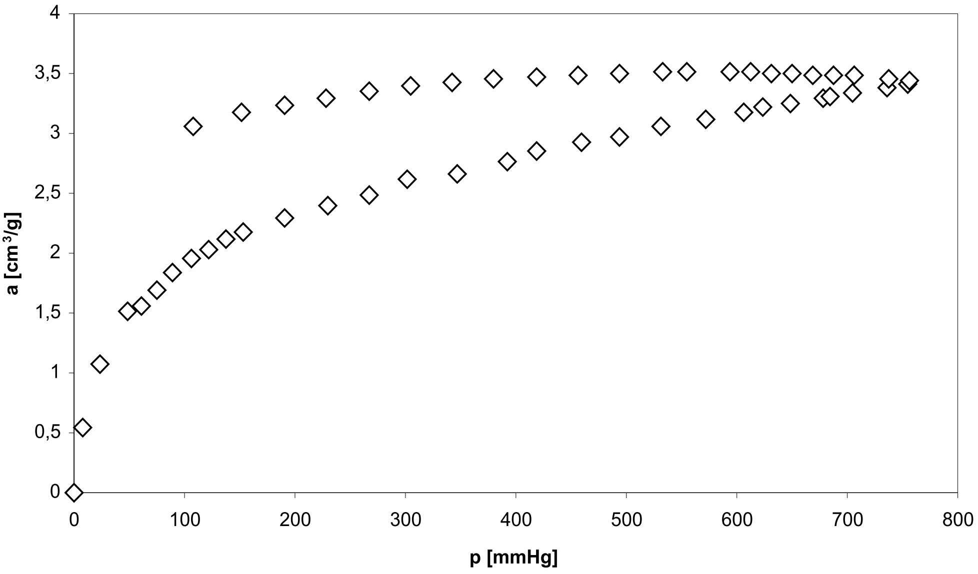

Fig. 5. Isotherms of propylene sorption/desorption on CW coal

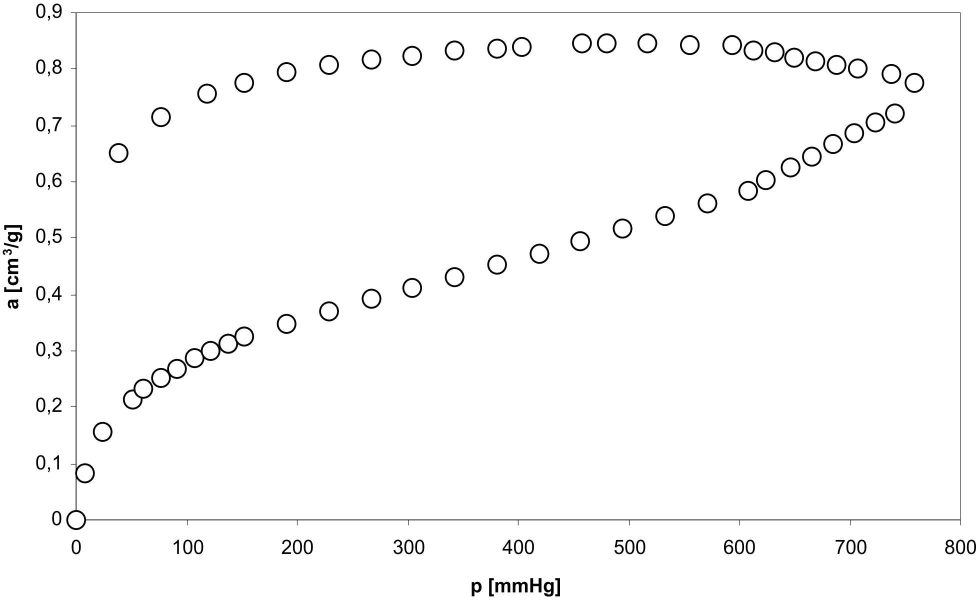

Fig. 6. Isotherms of propane sorption/desorption on CW coal

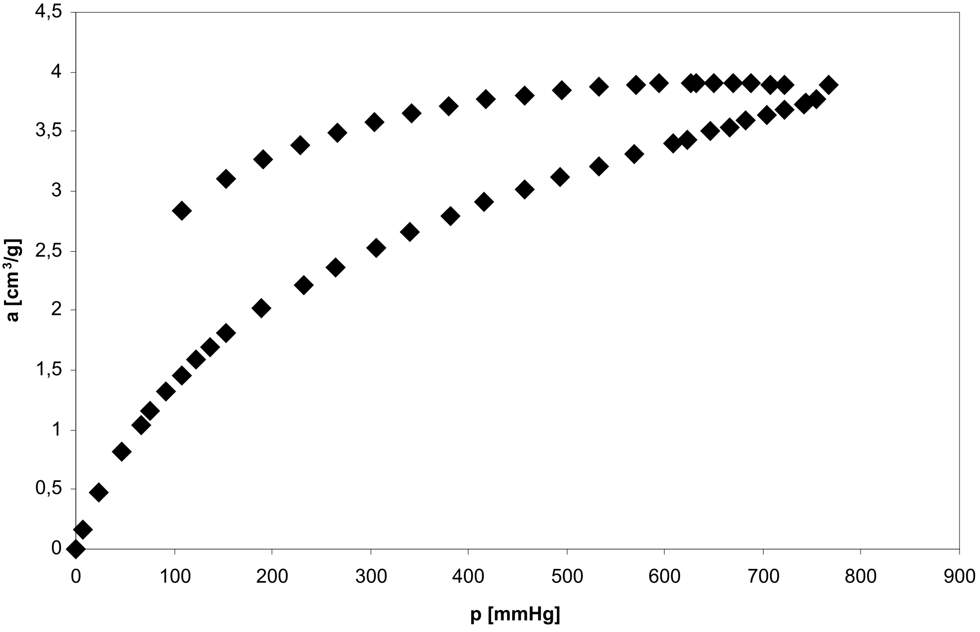

Fig. 7. Isotherms of ethylene sorption/desorption on CW coal

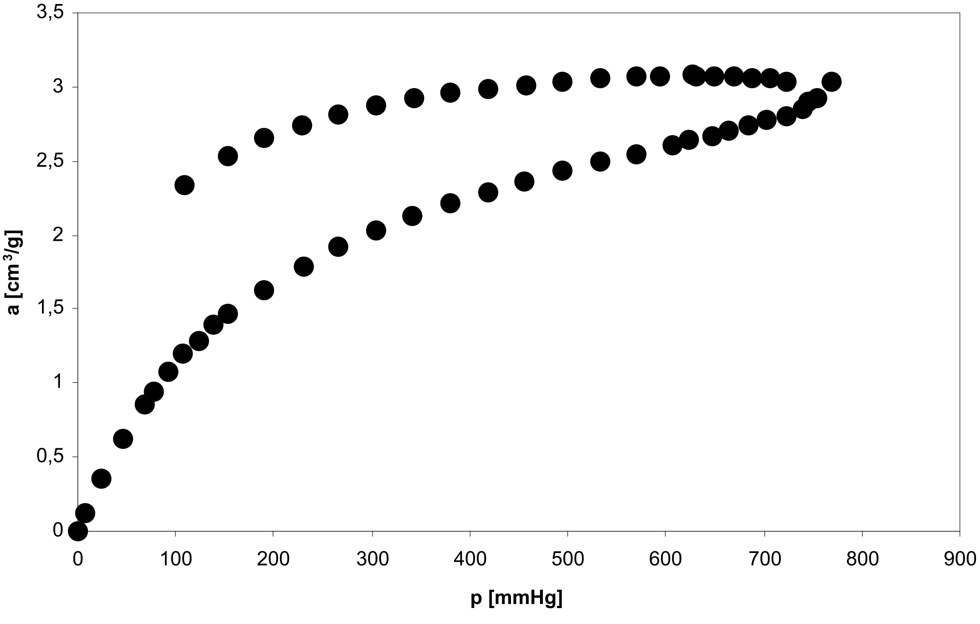

Fig. 8. Isotherms of ethane sorption/desorption on CW coal

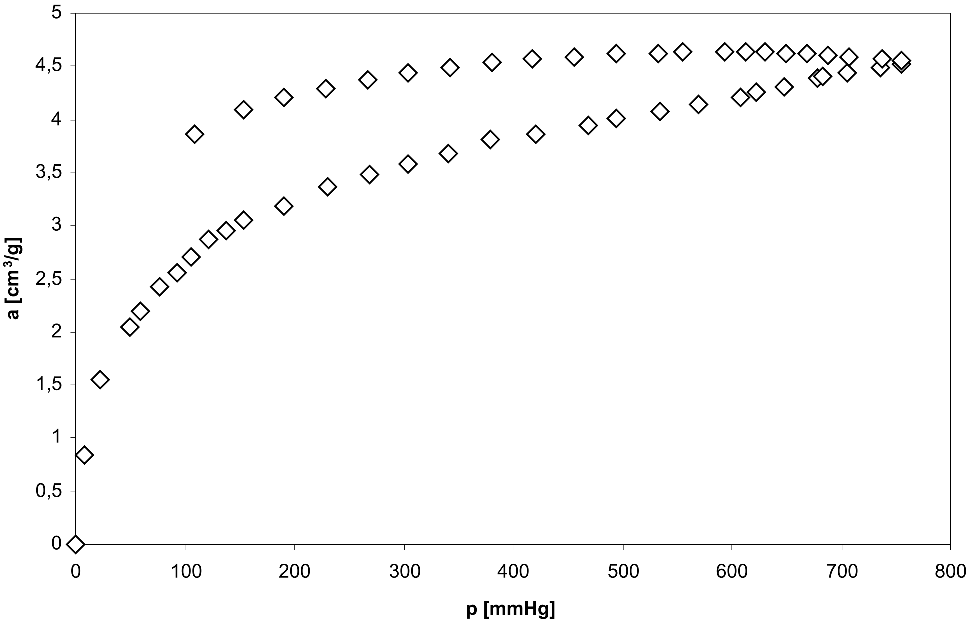

Fig. 9. Isotherms of propylene sorption/desorption on BB coal

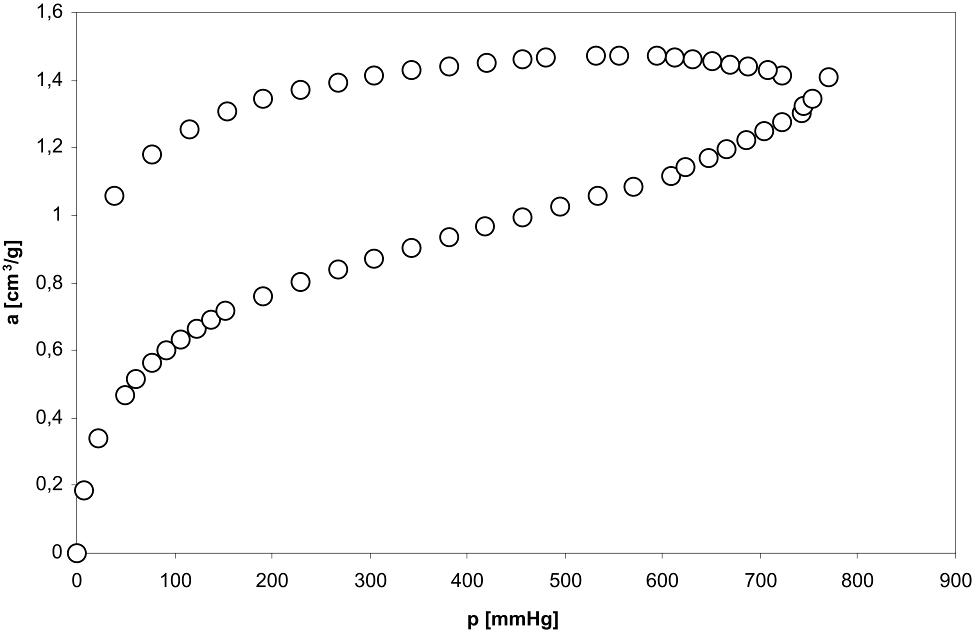

Fig. 10. Isotherms of propane sorption/desorption on BB coal

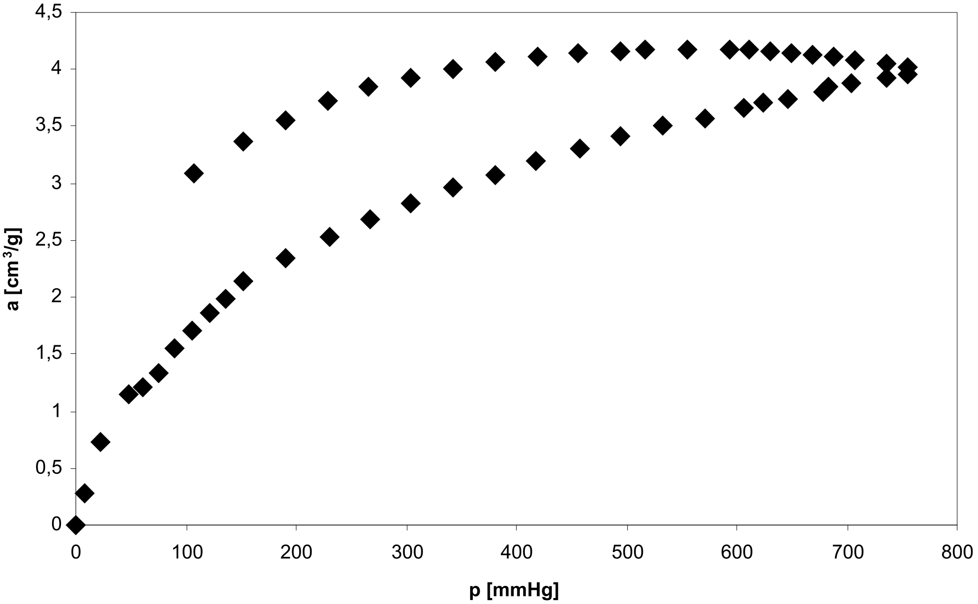

Fig. 11. Isotherms of ethylene sorption/desorption on BB coal

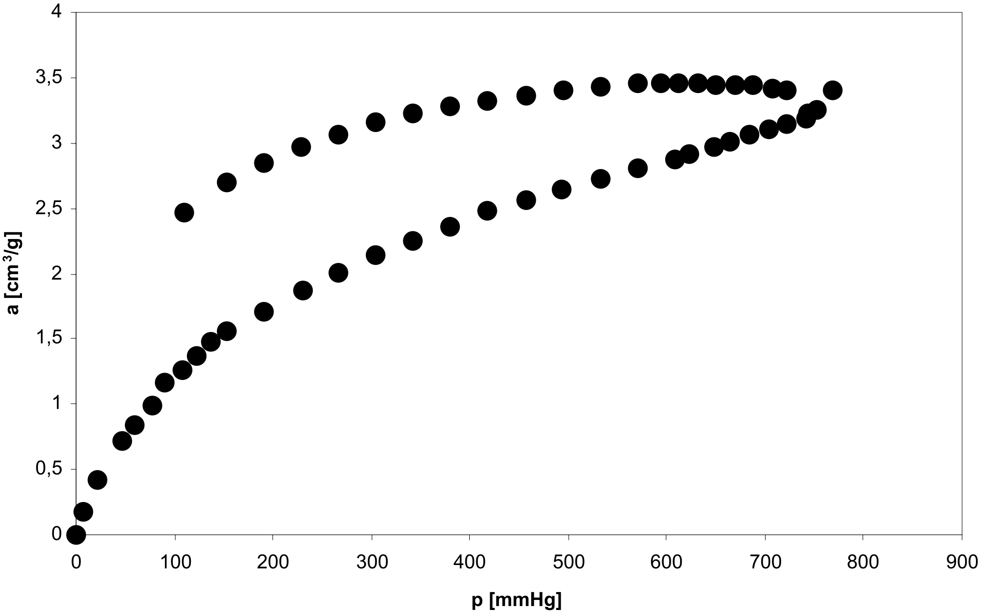

Fig. 12. Isotherms of ethane sorption/desorption on BB coal

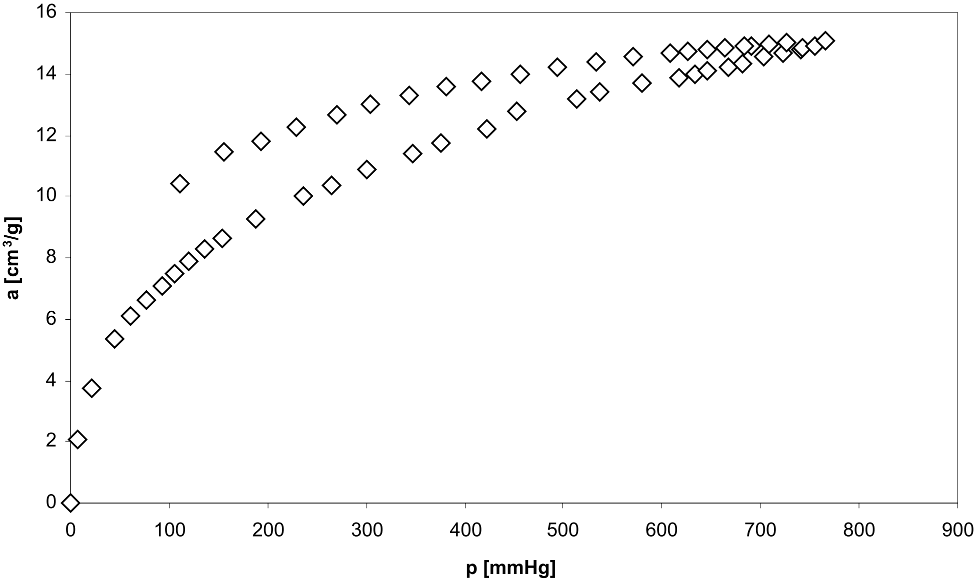

Fig. 13. Isotherms of propylene sorption/desorption on JW coal

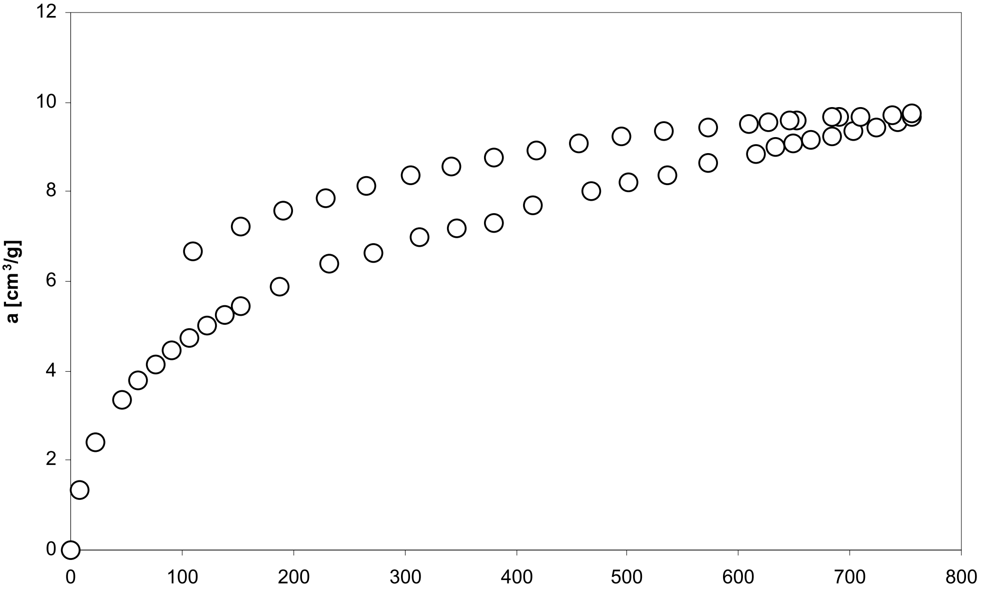

Fig. 14. Isotherms of propane sorption/desorption on JW coal

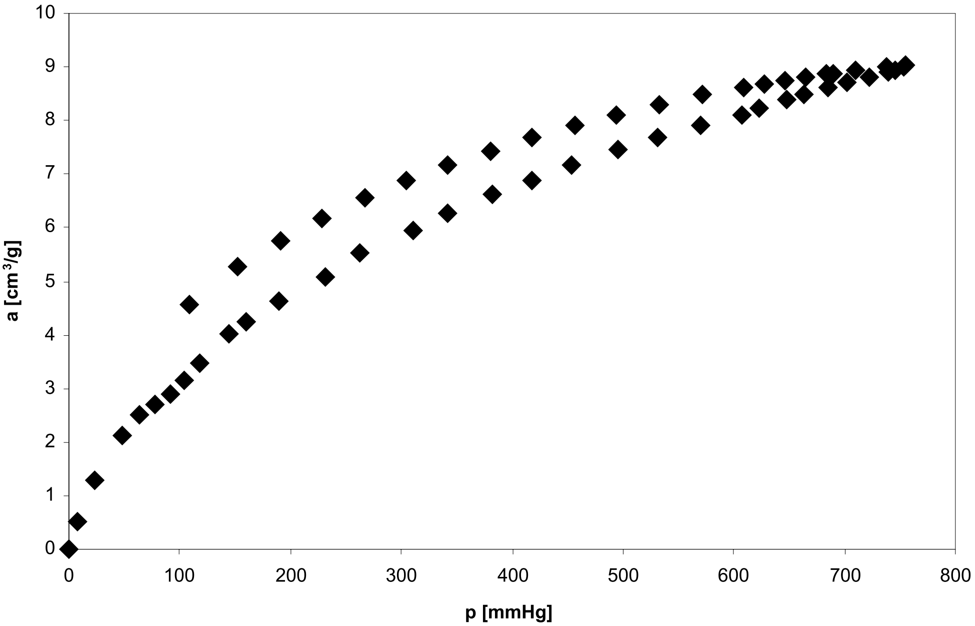

Fig. 15. Isotherms of ethylene sorption/desorption on JW coal

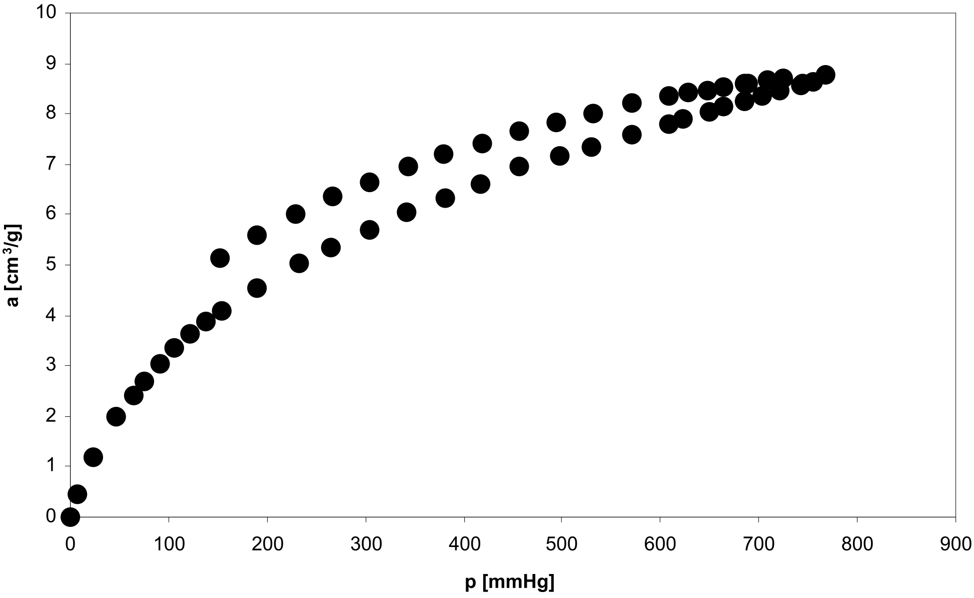

Fig. 16. Isotherms of ethane sorption/desorption on JW coal

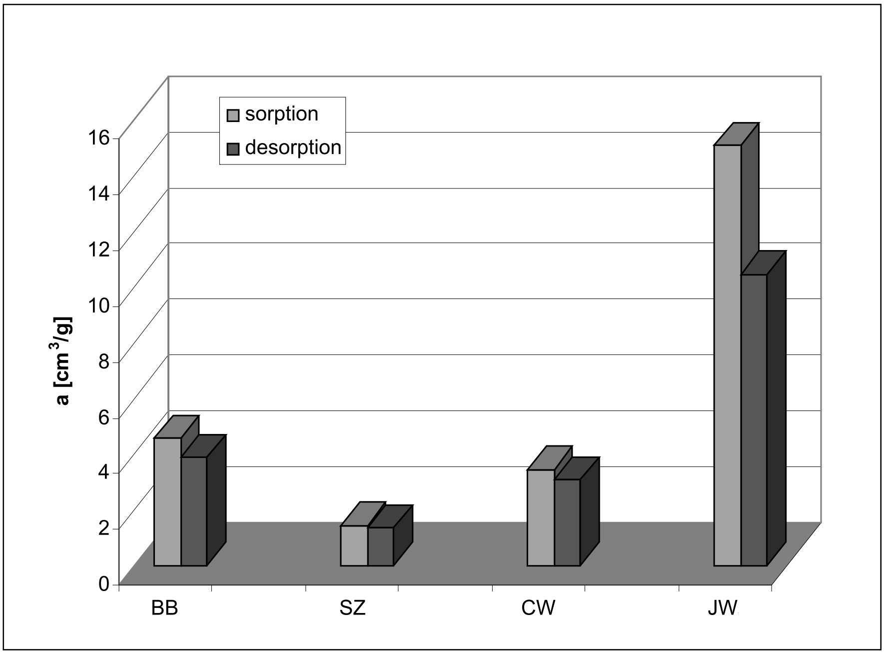

Fig. 17. Comparison of the possibility of sorption/desorption of tested coals to propylene

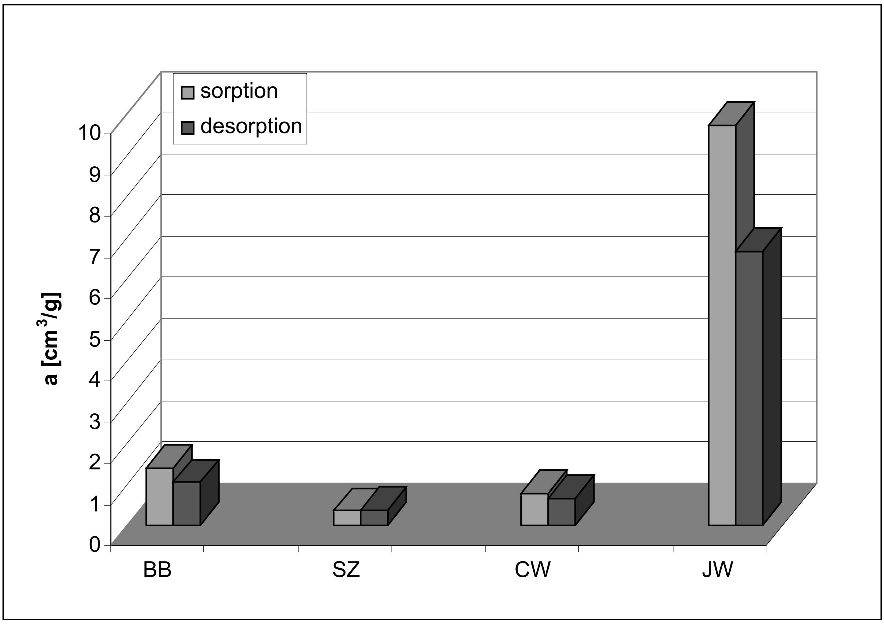

Fig. 18. Comparison of the possibility of sorption/desorption of tested coals to propane

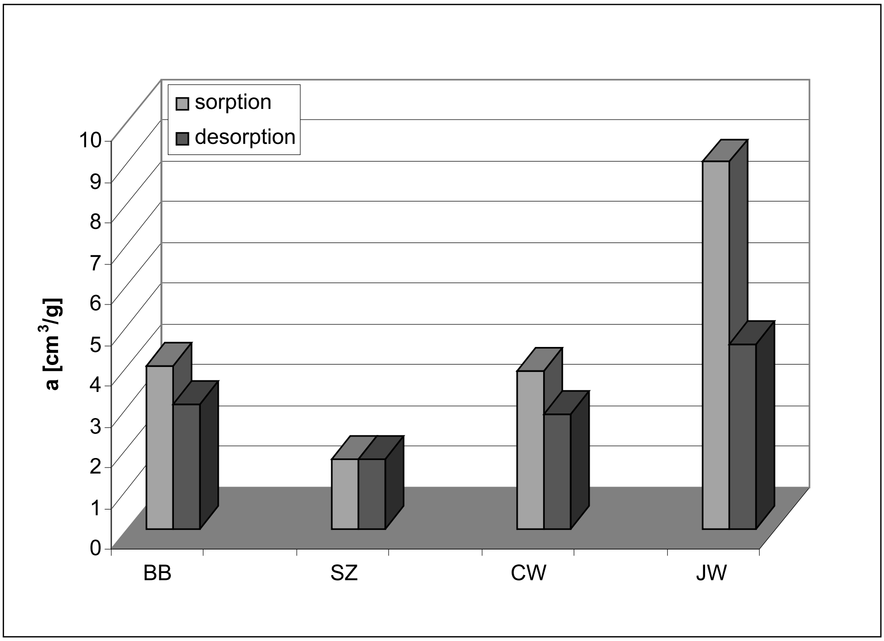

Fig. 19. Comparison of the possibility of sorption/desorption of tested coals to ethylene

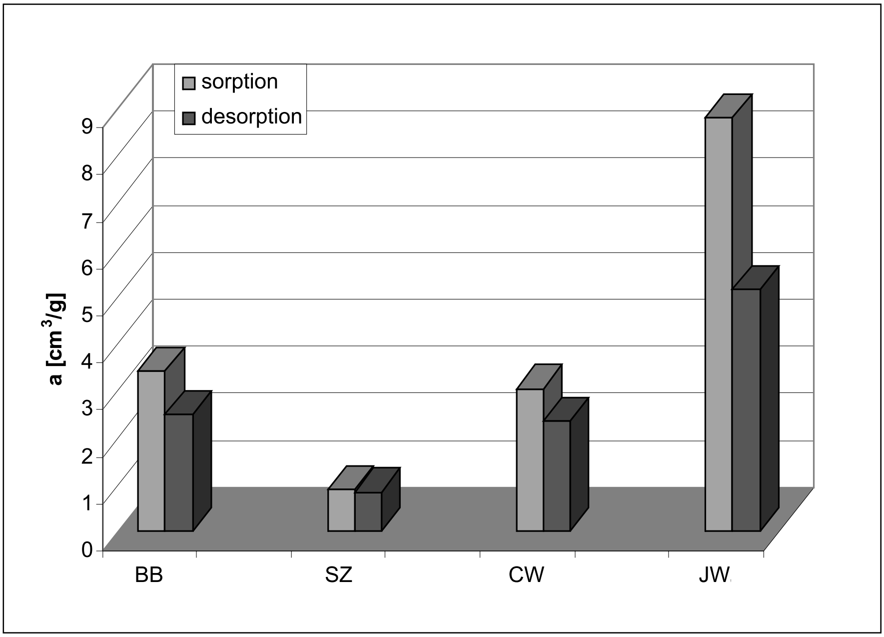

Fig. 20. Comparison of the possibility of sorption/desorption of tested coals to ethane

Lower values of sorption capacity with respect to ethane and propane are attributable to the lack of electrostatic interactions between condensed aromatic rings and totally apolar sorbate molecules. The analysis of sorption isotherms leads us to the conclusion that mexoporosity and microporosite play a dominant role in processes involving organic sorbates. Experimental tests reveal that sorption isotherms of hydrocarbon vapours on hard coal are irreversible in the investigated pressure and temperature range. In each case an open loop of hysteresis is revealed, indicating the predominance of sorption processes in the microporous coal structure.

4. CONCLUSIONS

Results of sorption/desorption tests supported by chemical and technological analysis of coal samples indicate an unambiguous correlation between the degree of metamorphism (elemental carbon and oxygen contents) and the sorption capacity value. For higher coal ranks and reduced oxygen content, the sorption capacity is reduced in the entire group of tested sorbents. It is reasonable to conclude that unlike sorption of polar substance, the sorption of vapours of apolar compounds involves mostly surface phenomena. It appears that the sorption process may also involve cracks and micropores in the surface layers in coal particles. Comparison of sorption/desorption isotherms reveals that differences in physico-chemical structure of hard coals, associated with their degree of metamorphism, influence the sorption capacity of the coal with respect to the same hydrocarbons. Most specific behaviour of the lowest rank coal sample with the higher porosity seems to be he consequence of a larger concentration of reactive functional groups and greater macropore volume than in remaining samples.

Experimental data reveal that the actual shape of sorption isotherms depends on coal and vapour types. Low values of sorption capacity registered for saturated hydrocarbons seem to confirm the dominating influence of the molecular sieve effect. It appears that in investigated systems the sorption process takes place mostly on the macropores' surface in coal. The higher sorption values for sorbates containing dual bonds may be attributable to possible association of non-saturated hydrocarbons on the surface of macropores. It is reasonable to suppose that sorption in investigated systems takes place mostly on the surface of macropores of the hard coal. Experiment results will give us a better insight into physico-chemistry of inter-phase processes in hard coals, contributing to the expertise gathered so far to support the prognostication of mining hazards.

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