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CO₂-ECBM AND CO₂ SEQUESTRATION IN POLISH COAL SEAM – EXPERIMENTAL STUDY

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ABSTRACT

Purpose	Methane recovery is interesting not only because of its clean combustion; it is also beneficial for the environment because of the reduction of the amount of methane emitted into the atmosphere, which is important because of methane's significant impact on the greenhouse effect. However, desorption of methane is a slow process, significantly dependent on the coalification of coal, its porosity and petrographic composition. Injection of carbon dioxide into the coal bed under sufficient pressure might be a factor in stimulating the efficiency of this process, as – because of preferential sorption – carbon dioxide displaces methane molecules previously absorbed in the coal matrix.
Methods	The measurements were made for Polish low-rank coal used for the analysis of methane recovery from Polish coal mines. Coal samples were collected from sites used for geological, sorption and petrographic research, as well as for the assessment of the reservoir's genetic origin CH ₄ content. Experimental studies of sorption were performed with the use of the volumetric method at a lower and higher gas pressure.
Results	The methane isotherms show more than double the reduction of adsorption along with increasing temperature. The most significant changes of sorption capacity due to temperature variations can be seen when observing the difference in the course of the hysteresis of sorption/desorption of the gas as a function of temperature. In cases where there is a temperature of 323 K, a temperature hysteresis loop might indicate larger quantities of methane trapped in the porous structure of coal. In cases of carbon dioxide as sorbate, a similar shape of sorption isotherms occurred at both temperatures, while the temperature increase caused approximately double the reduction of sorption capacity. Also the isotherm's shape is similar for both temperatures of measurement, indicating no effect of temperature on the amount of gas within the structure of the tested coal. High-pressure isotherms of CO ₂ and CH ₄ are confirmed in the literature, proving that carbon dioxide is the gas that allows the best penetration of the internal structure of bituminous coal. The critical temperature of CO ₂ (304.5 K) is so high, that sorption measurements can be performed at room temperatures (293, 298 K), where activated diffusion is relatively fast.
Practical implications	Understanding the sorption of gases is the primary issue, related to the exploitation of coal seams, when explaining the mechanism of gas deposition in coal seams and its relationship with outbursts of rocks and gases in mines.
Originality/value	The results indicate successful sorption of carbon dioxide in each experiment. This provides the rationale to study the application of the coal tested to obtain methane genetic origin genetic methane with the use of the CO ₂ injection.

Keywords

coal, sorption, sequestration, carbon dioxide, methane, ECBM

1. INTRODUCTION

When considering the possibility of CO₂ limitation, three options exist to reduce the total emission of CO₂ into the atmosphere i.e.: 1) reduction of energy intensity, 2) reduction of carbon intensity, 3) enhancement of CO₂ sequestration. Nowadays it is believed that carbon capture and storage

(CCS) technology is an obvious and priority candidate for long term technology policies and enhanced R&D efforts (Wdowin, Franus, & Panek, 2012).

Understanding the sorption of gases, related to the exploitation of coal seams, is essential when explaining the mechanism of gas deposition in the coal seams and its relationship

with outbursts of rocks and gases in mines. It is assumed, that the largest part of the gas within the coal seam is the methane which may be either in a free state (filling the pores and fissures), in the condensed surface phase (physical adsorption), or in the form of a molecular solution (absorption) (Crosdale, Beamish, & Valix, 1998). Methane recovery from coal seams based on natural gas desorption is related to safety issues, increasing environmental requirements (ozone layer, global warming, etc.) and the use of CH₄ from coal as an additional energy source. As an unconventional natural gas resource, coalbed methane receives worldwide attention. Coal seam gas is produced using methods and technologies adapted from the conventional oil and gas industry. Both primary (pressure) depletion and enhanced coalbed methane recovery (ECBM) methods have been tested for different pilot scales. In the ECBM process, non-hydrocarbon gases are injected to improve recovery of CH₄, either by stripping or displacement. In the case of displacement with CO₂ injection, one additional benefit is to simultaneously sequester carbon dioxide, if the geology and hydrology of the coalbed permit long term storage of injected gas (Mango, 2001; Harpalani, Prusty, & Dutta, 2006; Bachu, 2007; Prusty, 2008; Gentzis, Goodarzi, Cheung, & Laggoun-Defarge, 2008; Han, Sang, Cheng, & Huang, 2009; Ozdemir, 2009; Deisman, Mas Ivars, Darcel, & Chalaturnyk, 2010; Saghafi, 2010; Tarkowski & Wdowin, 2011; Zarębska, Baran, Cygankiewicz, & Dudzińska, 2012; Baran, Cygankiewicz, & Zarębska, 2013; Wdowin, Tarkowski, & Franus, 2013).

Laboratory and in situ studies prove that the secretion of methane from Polish coal seams is a slow process and there is a need to accelerate this process. Intensification of gas desorption depends mainly on the sorption properties of coal, seam characteristics (depth, state of stress), temperature, humidity and composition of the gas mixture influencing the coal. Recovery and utilization of methane is directly linked to the issue of occupational safety and health and environmental protection in mining. Uncontrolled emission of methane into air headings creates hazardous conditions in underground working places (outbursts, explosions, lack of oxygen, etc.). The principal difficulty of the studies is the preparation of relevant tests, as the results need accurate interpretation while also complying with the mining conditions. Therefore, the prediction of methane recovery from coal seams, based on the knowledge of the sorption/diffusion properties of coal obtained on the basis of the exchangeable sorption of CO₂ and CH₄ and mixtures of these gases, is of great importance. The study of the sorption process and its dependence on factors such as the structure of the sorbent, the nature of the sorbed substance and the conditions, in which the process takes place (eg, sorbate pressure progression) can be a model for methane drainage of exploited seams. The research of the coal-gas system is largely dependent on practical issues and remains in close connection with the material strength properties and changing permeability of coal seams. Such changes occur under the influence of the sorption of gases and vapors, when the coal is swelling and changing its mechanical properties. Sorption of mine gases brings about an increase of external dimensions of coal, and their desorption is accompanied by coal contraction. In spite of the fact that coals tends to sorb CO₂ much more effectively than CH₄, their deformation ability due to sorption is three times greater

during the sorption of carbon dioxide than for methane (Mazumder & Wolf, 2008). This is particularly important during the mining of coal in gas mines, because the injection of carbon dioxide to the coalbed containing methane may lead to increased stress in the rock strata as the coal will not be able to expand any further and this will cause changes to the seam permeability.

The main aim of the laboratory tests, presented in this study, was to find the relationship between the properties of subbituminous coal (porous structure, metamorphic stage, the petrographic composition) and the process of methane release. The impact of sorption of other gases (carbon dioxide) on the desorption of methane is a particularly important issue.

The broad spectrum of issues that arise during the implementation of the selected work requires the consideration of issues relating to the processes of sorption of gas mixtures and individual components on the basis of applied adsorption theories, coal composition and its porous structure.

The sorption process associated with the diffusion of sorbate in the sorbent structure is of a complex nature, because the transfer of the sorbed substances depends on both the sorbate and sorbent type, sorbent porosity and the conditions in which the process takes place. However, the analysis of experimentally obtained sorption isotherms faces difficulties due to the heterogeneous structure of porous sorbent, as well as additional mechanisms for the transfer of low molecular weight substances within the pores of the carbonaceous material (Charrière, Pokryszka, & Behra, 2010). According to the literature (Weishauptová & Medek, 1998), it is assumed that the gas is stored in the coal in four main forms: a) in the micropores, b) in the meso and macropores, c) as free gas in the free areas of meso and macropores, unoccupied by water, d) as gas dissolved in water. The interaction of water with natural coal is more complex than the interaction of non-polar gases like helium, methane or carbon dioxide. This complexity is due to the weak dispersion interaction of water with coal, the tendency of water to form hydrogen bonds with other sorbed water molecules and surface-chemical species, and the physisorptive interaction with the coal mineral matter. The sorption of water vapour and methane on coal surfaces is controlled by polar (e.g. carboxylic and hydroxylic) functional groups. Polar sites on the coal surface are preferentially occupied by water, hence reducing the capacity for CO₂ and CH₄ (and other gases) (Gensterblum, Busch, & Kross, 2014). Methane sorption capacity of coal is directly linked to the coal surface area, which is mainly made of micropores (Levy, Day, & Killingley, 1997; Crosdale et al., 1998; Pan, Connel, & Camilleri, 2010). Subsequently, the smaller part – in the form of adsorbed gas – binds on the surface of meso- and macropores, while the majority is free gas contained within the pores. This is directly linked with the conclusions of Gilman and Beckie (2000), stating that the total methane adsorption capacity increases with the increasing degree of coalification, thus coal rank is considered as the main parameter influencing the methane sorption capacity of coal (Bustin & Clarkson, 1998; Chalmers & Bustin, 2007; Busch & Gensterblum, 2011). This suggestion is based on methane adsorption capacity measurements of coal samples of varying metamorphic degree, ranging from subbituminous coal, through bituminous to anthracite (Gensterblum, Merkel, Busch, & Krooss, 2013). The results of the studies suggest,

that coals with a low degree of coalification (subbituminous coal), both durain and vitrain do not differ in terms of methane adsorption capacity; on the contrary, their capacities are similar (Crosdale et al., 1998; Crosdale, 2004). It should also be noted, that the volume of micropores is greater for bright coal samples; when compared to dull coal samples, the volume of micropores and the volume of methane does not increase with the increasing degree of coalification of low-rank (subbituminous) coal (Prinz & Littke 2005).

From a practical point of view, the problem of sorption and diffusion of gases in coal is associated with issues such as the transport of gases through the coal seam and the storage of molecules of gaseous or steam substance on the surface and within the coals, namely gas storage in seams and competitive sorption of gases from gas mixture. Such complex interactions in bituminous coal – low molecular weight substance (CO₂, CH₄) system are the reason why this topic is of great interest to researchers attempting to identify the structure of these sorbents and to describe the processes occurring within the coal matrix.

2. EXPERIMENTAL

2.1. Samples

The measurements were made for Polish low-rank coal used for the analysis of methane recovery from Polish coal mines. Coal samples were collected from sites used for geological, sorption and petrographic research, as well as for assessment of the reservoir's genetic CH₄ content. Table 1 and 2 show the characteristics of the test material.

Table 1. Petrography of the investigated samples (mmf = mineral matter free)

Sample	Sample interval [m]		Vitrinite (mmf)	Liptinite (mmf)	Inertinite (mmf)	Mineral matter	Vitrinite reflectance
	Top	Base	%	%	%	%	%
PR-1/7	1071.4	1071.8	71	6	23	3	0.72

Table 2. Summary of results from the analysis sample

Sample ID	A(a)	V(daf)	C(daf)	H(daf)	N(daf)
	%	%	%	%	%
PR-1/7	5.06	35.71	80.34	5.17	1.33

Parameters determined according to the following Polish standards: V, PN-81/G-045-04516; ash, PN-80/G-04512. Elemental analyses for H and C obtained using the Carlo Erba EA 1108 elemental analyser. A – ash content; V – volatile matter; C – carbon content; H – hydrogen content; N – nitrogen content; superscript daf – dry and ashless state, a – analytic state.

Samples were collected according to the PN-90/G-04502 standard, and then – in order to average physicochemical properties of the test material – the coal was hand-crushed, to measurement fraction of 0.5–0.7 mm. As specimens were prepared for the measurements, previously absorbed/adsorbed gases and vapours had to be removed from the coal surface and absorbed/adsorbed molecules had to be removed from the micropore. For that reason, coal specimens were evacuated in the conditions of vacuum, under 10⁻³ Pa. Before sorption measurements, hard coal samples were degassed at 318 K by being flushed several times with helium for the easier removal of vapors and gases previously adsorbed on the coal surface (Saha et al., 2007).

2.2. Sorption measurements

Experimental studies of sorption were performed with the use of the volumetric method at lower (I) and higher gas pressures (II). Low-pressure measurements used a sorptomat apparatus, ASAP 2010 (Micrometrics). A coal sample was subjected to an ever-increasing pressure of gas from the cylinder until equilibrium was reached. The study was performed at 298 and 323 K in low pressure up to 1 bar. The experiment was performed at two temperatures, because of the change of temperature in a coal seam during mining, which can vary by as much as several degrees, which significantly affects the balance of the coal – gas system. This is also accompanied by the change of gas pressure within the seam, and thus the quantity adsorbed by the coal. A description of the coal – gas system should take into account these phenomena, while sorption/desorption studies are among the methods which are most useful for understanding these processes.

Low pressure measurements use sorbates in the form of single gases: CO₂, CH₄ and their mixture (50% CO₂ + 50% CH₄). The purpose of this experiment was to compare the sorption capacity of coal with both carbon dioxide and methane. It is a widely accepted view that coal seams can be used as unconventional gas reservoirs (Moore, 2012). Unfortunately, current knowledge on both methane recovery from coal seams and the reverse process – storage of gas in seams – is still insufficient (Gensterblum et al., 2014). This follows from the fact that different factors affect different properties of the coal – gas system. However, it is generally accepted that typical coal mine gas is composed of 95% methane and other gases, while the most common component is CO₂. Thus, coal mine gas is a gas mixture, not the individual gas. When the sorption of single gas over a given area is considered, three parameters are sufficient: temperature, pressure and the quantity of sorbed gas. In the case of sorption of a binary mixtures of gases, it is necessary for the gas composition, during the sorbed phase, and the equilibrium content of the gaseous phase be known. So far, no universal model describing a mechanism for the extraction of methane from a coal seam is fully developed (Liu & Wilcox, 2012a, 2012b; Liu & Wilcox, 2011). At the same time, any test results that illustrate the interactions between coal and gas mixtures (CO₂ + CH₄) provide information that can be used to develop this issue. As mentioned above, the use of both sorbates and their mixtures comes from the fact that the extraction of methane from coal seams could be enhanced with the use of CO₂ sorption, during its injection into the seam.

High-pressure measurements were performed with two measuring methods. For CO₂, sorption studies were performed with the use of a volumetric method, pressure of up to 3 MPa and at a temperature of 298 K using the original apparatus designed and built at the Department of Energy and Fuels AGH (Baran, Broś, & Nodzeński, 2010; Macuda, Nodzeński, Wagner, & Zawisza, 2011).

High-pressure methane excess sorption isotherms of up to 17 MPa were conducted at 306 K after moisture-equilibrating the coal samples according to the ASTM 1412 procedure. (High-pressure studies were performed on behalf of the Institute of Geology and Geochemistry of Petroleum and Coal RWTH Aachen University by Philipp Weniger and Bernhard

Kross). Further information on the experimental procedure is given by Busch, Gesternblum, Kross, and Simons (2006). High-pressure sorption studies provide the necessary data on the tested coal, depending on the nature of gas and its pressure. This is related to the fact that the coal mass in the seam is under the influence of the gas that diffuses through its deeper layers to the head, while the exploitation of gas-bearing seams with mineshafts and tunnels is accompanied by a high risk of outburst. Within the tunnels located outside the seams, methane release depends on the amount of free methane being released from the fractured side of the excavation site. When approaching the face, an additional amount of methane is released, extracted from the stress-relieved zone. The gas pressure gradient existing between the seam and the excavation results in the transfer of gas into the excavation. The factor that determines the size of this additional flow is the methane-bearing capacity of the seam, which is the amount of gas saturation. The balance of coal-gas system changes with the changes in gas pressure. Therefore, the experiments presented in this study were performed with the use of the two aforementioned methods.

3. RESULTS

Figures 1 and 2 show the low-pressure sorption/desorption isotherms of methane at the temperature of 298 and 303 K. The curves show more than double the reduction of adsorption along with increasing temperature. What is more, a change in the shape of the isotherms is clearly visible. At a temperature of 298 K the isotherm's shape corresponds to a type I isotherm according to the IUPAC (Langmuir curve), while at a temperature of 323 K the curve takes the shape of a type II isotherm. The difference in the course of the hysteresis of sorption/desorption of the gas as a function of temperature is also noteworthy. In cases with a temperature of 323 K, the temperature hysteresis loop might indicate larger quantities of methane trapped in the porous structure of the coal. In light of the polymeric model of coal, any consideration of the properties and behavior of the sorption system should take into account coal porosity since the gas deposit mechanism is closely related to the size of the pores.

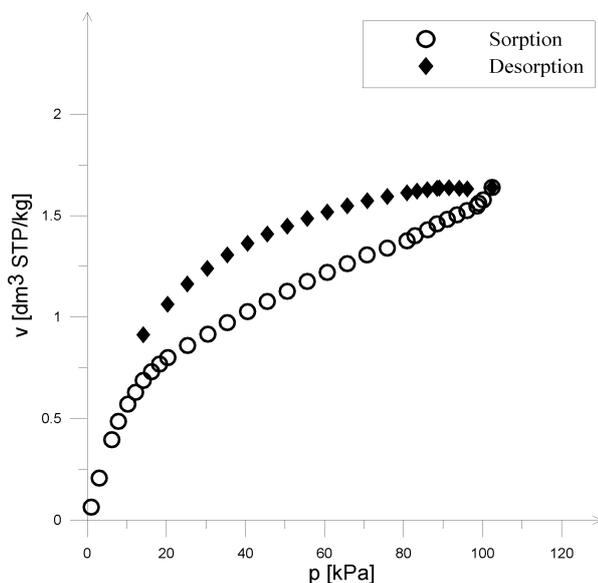


Fig. 1. Low pressure isotherm sorption/desorption of CH₄ at 298 K

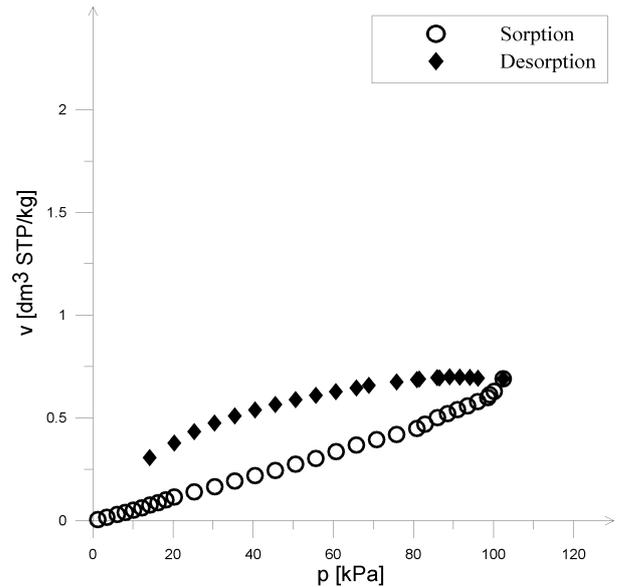


Fig. 2. Low pressure isotherm sorption/desorption of CH₄ at 303 K

In low rank coals – due to the existence of elements with large dimensional variation within their structure – there is, relatively, the biggest amount of mesopores between the side chains. Meanwhile, the lowest volume is attributable to the pores with dimensions of sorbate molecules, which is why these coals have a lower volume of the flexible absorbent phase than other coals.

Figures 3 and 4 illustrate low-pressure CO₂ sorption. In cases of carbon dioxide as sorbate, a similar shape of sorption isotherms occurred at both temperatures, while the temperature increase caused approximately a reduction of double the sorption capacity. Also the isotherm's shape is similar for both temperatures of measurement, indicating no effect of temperature on the amount of gas within the structure of the tested coal. A comparison of the two sorbates curves shows a CO₂ sorption capacity which is two times higher. When looking at a sorption of gas mixtures of CO₂ and CH₄, with a composition of 50% plus 50% (Fig. 5, 6), the obtained sorption capacity values were half that of CO₂ as a single sorbate and almost double that of CH₄. This is confirmed in the literature (Garnier et al., 2011), while the differences between physicochemical properties of sorbates are primarily responsible for such a course of the isotherm.

The observed course of the sorption curve of the mixture in a bimodal pattern of coal may be the result of the blocking of conical and fissured pores by CH₄ molecules. Carbon dioxide molecules are linear and non-polar, as the opposite dipolar moments of the oxygen-carbon bonds are equilibrated. On the other hand, they are characterized by a high quadrupole moment, which might alter the mutual interactions with the heterogeneous centres of the structural elements of the carbon substrate. The CH₄ molecule is tetrahedral and apolar in nature, hence the role of its dispersive properties in interactions with the carbon material is considerable. The shape of desorption isotherm of the mixture which indicates almost two times higher value of the gas/mixture stored in the structure of the sorbent is also noteworthy. The study results – confirmed by earlier studies – confirm that CO₂ sorption of binary gas mixtures is the preferential type of sorption. Also in this case, a temperature increase is responsible for the

reduction of the sorption capacity, but the hysteresis loop shows the positive impact of temperature increase on the efficiency of the desorption process.

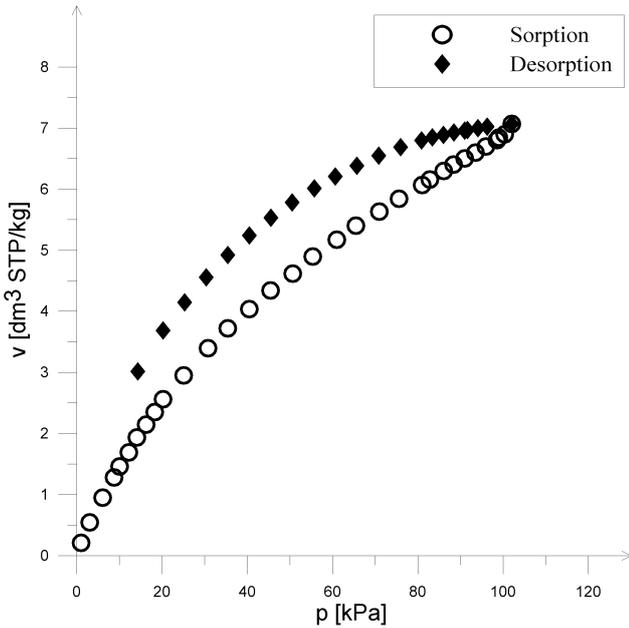


Fig. 3. Low pressure isotherm sorption/desorption of CO₂ at 298 K

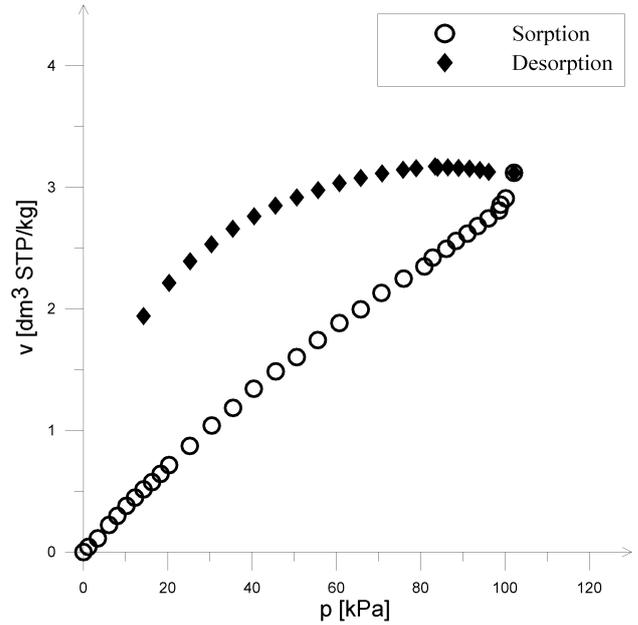


Fig. 5. Low pressure isotherm sorption/desorption of CH₄ and CO₂ mixture at 298 K

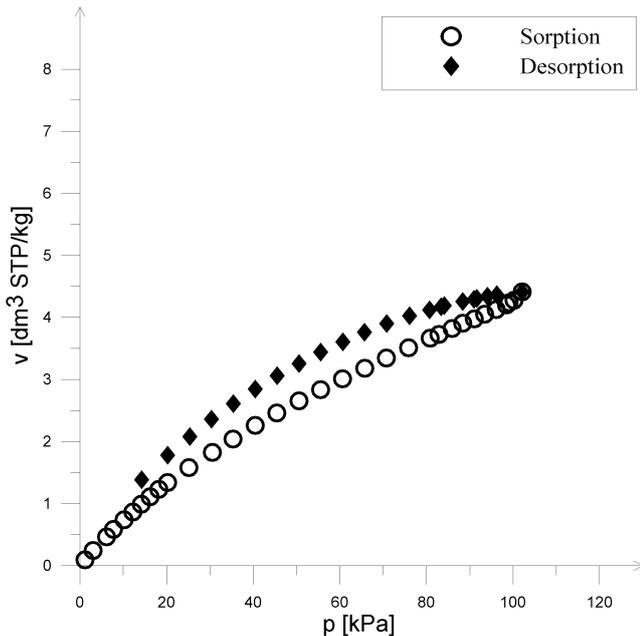


Fig. 4. Low pressure isotherm sorption/desorption of CO₂ at 303 K

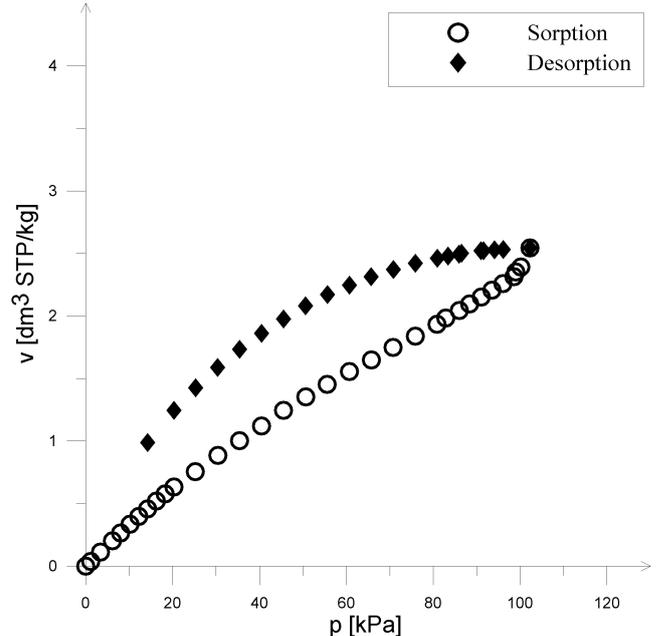


Fig. 6. Low pressure isotherm sorption/desorption of CH₄ and CO₂ mixture at 303 K

Based on sorption isotherms drawn for individual sorbates of CO₂ and CH₄ (Fig. 7, 8) it is reasonable to say that although they have a similar shape, throughout the whole tested range of pressures, methane sorption capacity of both coal types is almost twice as low than that of carbon dioxide sorption capacity. This is in close connection with kinetic energy, sorbates particle size, their shape and the polar nature of the CO₂ molecule (the presence of quadrupole moment) and the non-polar nature of the spherical particle of CH₄ (Table 3).

Table 3. Selected properties of CO₂ and CH₄

Parameter	Unit	CH ₄	CO ₂
Molar mass	g/mol	16.04	44.01
Critical pressure	MPa	4.64	7.38
Critical temperature	K	190.56	304.21
Normal boiling point	K	111.67	194.75
Critical density	g/cm ³	0.163	0.466
Kinetic diameter	nm	0.380	0.330
Critical diameter	nm	0.40-0.42	0.28-0.37
Dipole moment	D	0.0	0.0
Quadrupole moment	erg ^{1/2} ·cm ^{5/2}	–	4.3·10 ⁻²⁶

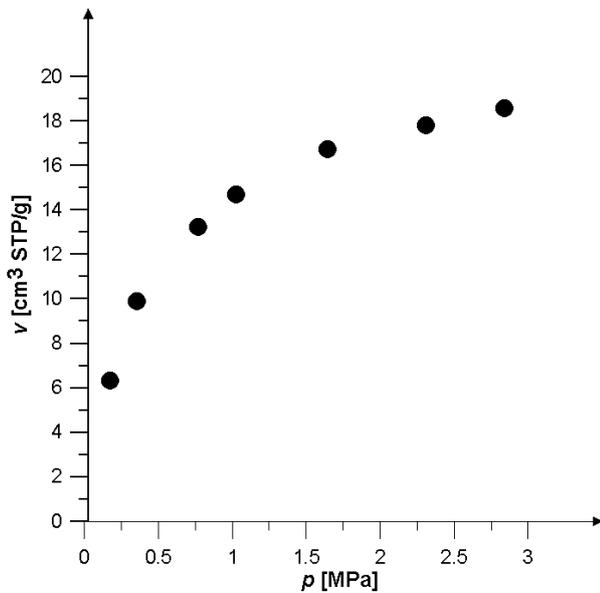


Fig. 7. High pressure excess isotherm sorption of CO₂ at 298 K

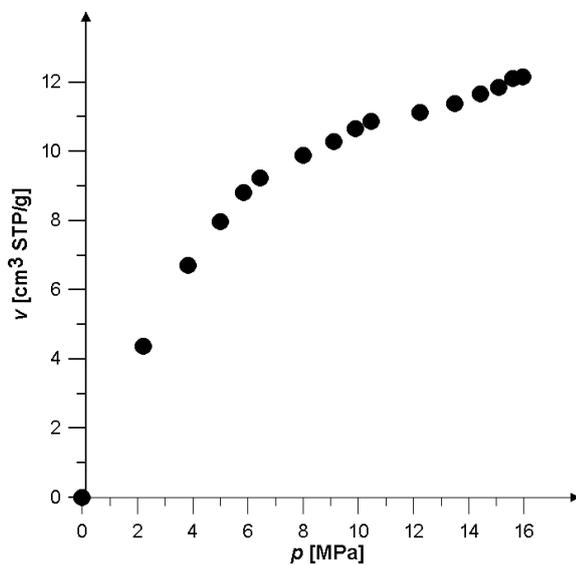


Fig. 8. High pressure excess isotherm sorption of CH₄ at 298 K

These factors are responsible for (both proven in the literature and during the study) higher value of the CO₂ sorption capacity (Li et al., 2010). CH₄ molecule in the gas phase has a large kinetic energy, therefore in the initial period of contact between the sorbate and the coal, penetration of the coal molecule with gas takes place relatively quickly, while an exceptionally stable molecule of methane of spherical construction initially penetrates the pores of coal, where it is the subject of physical adsorption (Yu et al., 2008). At temperatures higher than the critical, condensation of methane in the pores is unlike to occur, while the density of the adsorption layer may be relatively high depending on the pressure and the diameter of the micropores (Mosher, He, Liu, Rupp, & Wilcox, 2013). The methane molecule is characterized by the low polarity of bonds and therefore in the process of coal – the decisive role of methane interactions is played by dispersion force. Meanwhile, the reduction in CO₂ sorption capacity could indicate that some of the pores are not available for methane molecules, as penetration by the molecules of this sorbate demands considerable energy in order to spread

their walls (Cui, Bustin, & Chikatamarla, 2004). The longer the coal samples interact with the methane (which is increased by the saturation of the adsorption space, vibration of the coal copolymer network elements and the presence of flexible phases), more and more areas of coal – which initially did not participate in coal-gas interactions – are penetrated by the spherical molecules of methane (Zarębska & Ceglarska-Stefańska, 2006).

High-pressure isotherms of CO₂ and CH₄ are confirmed in the literature, proving that carbon dioxide is the gas that allows the best penetration of the internal structure of bituminous coal. The critical temperature of CO₂ (304.5 K) is so high, that sorption measurements can be performed at room temperatures (293, 298 K), where activated diffusion is relatively fast. A molecule of carbon dioxide – in the absence of the permanent dipole moment – is characterized by the presence of a quadrupole moment, which determines the increase of the energy of the interactions between the particle and the solid surface (if there are electric charges concentrated on its surface) (Mosher et al., 2013). In addition, the small size and low activation energy of the gas molecules allows for good penetration of the structure of the coal substance (Pan, Luke, Connel, & Camilleri, 2010). The shape of the isotherm – at the lowest given pressure – may indicate that the initial sorption process takes place only on the surface, which is followed by the process of volumetric filling of the sorption space. The increase of the energy of adsorption in micropores leads to the rapid increase in the value of adsorption at low pressure, which is reflected in the large inclination of the initial section of the isotherm.

The measurements were performed at 298 K, which is below the critical conditions for carbon dioxide. Collected in an absorbing phase and flexible absorbing phase, sorbate may have a density close to the density of the liquid, while the sorbate located in the coal copolymer network, which fills its volume, acts like a lubricant between the elements at higher pressures. It should be noted that the values of specific surface area derived from the measurements of CO₂ sorption at 298 K are consistent with the values obtained for the same coals with the use of X-ray scattering at small angles (Karacan & Mitchell, 2003). It can be concluded, that in terms of the relationship between the capillary structure and sorption properties of porous material within subbituminous coal, micropores are the most important feature.

4. CONCLUSIONS

The process of sorption/desorption of methane and carbon dioxide depends on both the type of gas and the properties of studied coal samples. The process of gas release from coal depends on the capillary structure, significantly determined by the porosity and the maceral composition of the coal. The data presented can be applied to actual mining conditions, often accompanied by a rapid outcrop of coal-containing gas, which causes system instability, rapid desorption, the lowering of temperature and retention of gas in coal. The gas – depending on conditions, the capillary structure and the permeability of the coal bed – can be slowly released or produce relatively high pressure within the capillaries. Lower values of methane sorption, when compared with carbon dioxide, determine – at a given pressure – the possibility of increasing the gas release during CO₂ injection. Smaller mo-

lecules are sorbated faster than larger ones, according to the mechanism of kinetic resolution. This effect is strongest at lower pressures, when the sorption space is clean (degassed) (Chaback, Morgan, & Yee, 1996; Cui et al., 2004). Both sorption capacity and stability depend on the individual sorbate's ability to overcome the energy barrier associated with the process of diffusion through narrow ultramicropores. The narrow entrances to the micropores in bituminous coal are comparable with the diameters of methane molecules. Therefore, this gas needs more time to penetrate the sorption space, this is necessary to reach equilibrium sorption. In contrast, CO₂ molecules have good access to all pores with radii larger than 0.271 nm, and therefore only carbon dioxide is able to penetrate all ultramicropores (Charrière et al., 2010). A carbon dioxide sorption capacity of coal, which is twice as high, allows for intensified methane extraction and the simultaneous storage of CO₂.

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