



Original Paper

Sorption and Desorption of CO₂ and CH₄ in Vitrinite- and Inertinite-Rich Polish Low-Rank Coal

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Low-pressure sorption tests were carried out on samples of selected Polish bituminous coal in coal–methane and coal–carbon dioxide systems. The purpose was to determine the relationship between the petrographic composition of low-rank coal and the amount of gas stored in its porous structure and desorbed from it. The influence of the degree of coalification on the amount of sorbed gas was reduced to minimum, because isotherms of deposition and evacuation of gases were determined on the base coal samples and two concentrates of lithotypes, vitrain and durain, isolated from the original coal. It was found that the sorption capacity of carbon dioxide was related to the petrographic composition, but no such correlation was observed in regard to methane. Langmuir and Dubinin–Radushkevich sorption isotherms and the modified desorption model based on Langmuir equation were chosen. The applied equations gave a very good fit to the experimental data. Calculated parameters corresponding to free adsorption energy in the Dubinin–Radushkevich equation allow concluding on the independence of its mechanism from coal petrography and on the preference of carbon dioxide sorption. Calculated adsorption equilibrium constants in Langmuir’s equation show variability with petrographic composition of coal and have lower values for methane than for carbon dioxide. It was shown that the size of the hysteresis loop depends on the petrographic composition of coal and increases with increase in vitrinite content for both sorbates, which was confirmed by values of areal hysteresis index and hysteresis parameter.

KEY WORDS: Hard coal, Lithotypes, Macerals, Methane, Carbon dioxide, Sorption isotherm.

INTRODUCTION

Studies on sorption of mine gases, carbon dioxide (CO₂) and methane (CH₄) on hard coal serve as bases for investigations of several issues concerning the transport of gas in coal beds. The issues include the storage of gases in coal seams, CO₂ sequestration, extraction of CH₄ from coal beds along with the enhanced CH₄ with CO₂ injection as

well as the outbursts phenomena, namely a spontaneous coal, gas and rock ejection, and self-heating of coal. Hence, there is a continuous increase in the number of works in this research field, both on a laboratory scale and in pilot installations. Several of them cover the analysis of changes caused by coal–gas interactions (CH₄, CO₂) in coal beds, including the explanation of their mechanisms and the development of analytical and numerical methods, tools to describe and model their course (Karacan and Mitchell 2003; Busch et al. 2004; Czerw and Ceglarska-Stefanska 2008; Zarębska and Dudzińska 2008; Maphala and Wagner 2012; Baran et al. 2014; Mavhengere et al. 2015; Skoczylas et al. 2015; Czerw

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et al. 2016; Kudasik 2016; Skoczylas and Topolnicki 2016; Kudasik 2017; Baran et al. 2018a, b; Macuda et al. 2020).

Coal is a combustible sedimentary rock of organic origin, mainly phytogenic. Its origin, specification of coalification process and technological properties are the areas of interest of coal petrology. The diversity of initial organic material, complexity and multi-directionality of coal-forming processes are the reasons for the heterogeneity of hard coal and its physicochemical and technological properties. The formation of coal deposits is a two-stage process. In the first, biochemical phase, accumulated organic matter is covered with rock sediments deposited by wind and water, often flooded with water (peat bogs) and transformed into humic acids through metabolism of aerobic and anaerobic bacteria. In the second, geochemical phase, after peat has been covered with a layer of impermeable sediment, the dynamic and thermal processes take place. Under the influence of geological factors, temperature and pressure, the content of carbon (C) gradually increases and the share of oxygen (O) and hydrogen (H) in coal decreases with simultaneous detachment of water molecules H_2O , CO_2 and CH_4 from coal matter and, in the case of anthracites, hydrogen molecules (H_2). At the second stage, a microporous coal structure is formed, capable of retaining some of the gases in the deposit. The composition and quantity of mine gases are also influenced by the properties of the sediments covering the deposit, including the influence of erosion of the overburden rocks and tectonic phenomena. Mine gases are a mixture with dominant components of CH_4 , CO_2 or N_2 and H_2O vapor in different concentrations. Mine gases are present in deposits and rocks of an overburden in the free-state in macro-pores and fissures, as gas can be adsorbed in micropores and in the structure of coal, as well as dissolved in water (Weishauptová and Medek 1998). The amount of gases occurring in particular forms is determined by the temperature and pressure in the deposit, the properties of coal and the nature of gas (Czapliński 1994).

Coal petrography is a part of petrology that includes the study and description of concentrated accumulations of coalified matter on a macroscopic and microscopic scale. Elementary petrographic components of coal are macerals. Their classification and systematics were prepared according to the differences in technological and optical properties. Hence, their petrographic

scheme and nomenclature are based on morphological aspects and not genetic characteristics. In part, however, the form and structure of macerals can be referred to a specific plant organ or tissue, or the process determining their structure (Wagner et al. 2008). In general, tissue parts of plants were transformed into macerals of vitrinite group; in turn, plant products resistant to oxidation (leaf epitelium, spores, seeds, resins and waxes) and primitive aquatic plants and zooplankton were placed into a group called liptinite, whereas inertinite group originally included components that were neutral in the coking process, rich in element C (carbonated, secondary oxidized or gellified components, remains of fungi). The main parameter for classifying the degree of coalification of hard coal is the coefficient of average reflectance of vitrinite, which ranges from 0.5 to 1.0% for low-carbon hard coal, 1.01 to 3.0% for medium- and high-carbon hard coal and 3.01 to 6.0% for anthracite (ISO 11760 2005).

Four basic lithographic separations of hard coal were distinguished based on macroscopic lithographic features of factual and petrogenetic dimension, so called lithotypes (Wagner et al. 2008; Bielowicz 2012; O'Keefe et al. 2013). Vitrain, also called bright coal, is mostly composed of macerals of the vitrinite group. It is characterized by black color, glassy luster and brittleness. Durain, a dull coal, is firm and hard, ranging in color from dark gray to black and consists mainly of macerals of the inertinite and liptinite groups. Clarain, a semi-bright coal, is an intermediate form between the two lithotypes described above and is the most common one. Its structure consists of alternating layers of vitrain, durain and fusain. Fusain, a fibrous coal, has a characteristic satin gloss, resembling that of charcoal. It consists mainly of two macerals of the inertinite group: fusinite and semi-fusinite. Differences in maceral composition among lithotypes result in differences in their physicochemical properties (Mastalerz et al. 2010; Teng et al. 2017). Inertinite and liptinite show higher meso-porosity and lower microporosity than vitrinite derived from the same coal or coal with similar degree of coalification (Clarkson and Bustin 1999). Differences in pore volume distribution and pore dimensions affect the sorption properties of coal (Wierzbicki et al. 2019).

Teng et al. (2017) compared the porosity of lithotypes separated by hand from three high-rank coals. Their study included low-pressure sorption of CO_2 , which gave insight to the structure of micropores. It was shown that surface area of micropores

and volume of micropores, calculated based on Dubinin–Radushkevich's isotherm, decreased in order from vitrain, through clarain and durain, to fusain. Sorption properties of lithotypes show the same general trend (Lamberson and Bustin 1993; Karacan and Mitchell 2003; Mastalerz et al. 2004, 2008).

The results of studies on sorption of mine gases carried out on different types of coal can be compared according to different criteria. The most basic is the influence of two factors on sorption properties of coal: the coalification degree (Juntgen and Karweil 1966; Gan et al. 1972; Yee et al. 1993; Clarkson and Bustin 1996; Levy et al. 1997; Bustin and Clarkson 1998; Prinz et al. 2004; Prinz and Littke 2005; White et al. 2005) and the petrographic composition of coal (Faiz et al. 1992; Crosdale and Beamish 1993; Lamberson and Bustin 1993; Clarkson and Bustin 1996; Bustin and Clarkson 1998; Crosdale et al. 1998; Clarkson and Bustin 1999; Laxminarayana and Crosdale 1999; Carroll and Pashin 2003; Mastalerz et al. 2004; Hildenbrand et al. 2006; Faiz et al. 2007; Weniger et al. 2010; Weishauptová and Sýkorová 2011; Weishauptová et al. 2015). The optimal option is to consider both of these factors in the analysis or to select a proper test material to eliminate the impact of either rank or maceral composition. A general conclusion can be drawn from studies carried out to investigate the relationship between the maceral composition of coal and its sorption properties. That is, an increase in macerals of the vitrinite group correlates with an increase in sorption capacity in relation to CO₂ (Mastalerz et al. 2004) and CH₄ (Beamish and Gamson 1993; Lamberson and Bustin 1993; Levine 1993; Bustin and Clarkson 1998; Chalmers and Bustin 2007).

Mastalerz et al. (2004) carried out a series of sorption experiments on low-rank coals from one seam (R_o values of 0.49–0.62%) using CO₂ and CH₄ as sorbates. They concluded that the CO₂ sorption capacity of coal is positively correlated with the content of macerals of the vitrinite group, whereas it decreases with increase in the content of macerals of the liptinite group. However, in the case of CH₄ they showed that there is no dependence of the sorption amount and the degree of coalification and petrographic composition of coal. Mastalerz et al. (2004) explained that differences in the sorption capacity of coal in relation to CO₂ and CH₄ result from the differences in sizes of CO₂ and CH₄ molecules and differences in the mechanism and energy of sorption of these gases. Smaller kinetic diameter and higher

adsorption energy of CO₂ mean faster and deeper diffusion and enable CO₂ molecules to penetrate the porous structure of coal more easily than CH₄. Moreover, it was found that CH₄ is almost exclusively adsorbed on micropores, while CO₂ is adsorbed and absorbed, and the share of the second mechanism can reach half of the amount of gas stored in coal. These conclusions are in accordance with other studies conducted in this field, for example those of Reucroft and Sethuraman (1987) and Milewska-Duda et al. (2000).

Busch et al. (2004; 2006) studied the sorption of mixtures of CO₂ and CH₄ on hard coals of a wide range of ranks. They observed that preference of sorption depends on degree of coalification, maceral composition of coal and dosing pressure of sorbate, but not on sorbate composition. Their study showed that high rank of coal is associated with preferential sorption of CO₂. In case of coals with low rank, there was no general trend, namely some samples preferentially sorbed CO₂ and others CH₄. In the related literature, studies indicated unambiguously the occurrence of preferential CH₄ sorption (e.g., Crosdale 1999; Majewska et al. 2009) as well as the selectivity of CO₂ sorption among mixtures of CO₂ and CH₄ (e.g., Ceglarska-Stefanska and Zarebska 2006; Yu et al. 2008; Pajdak et al. 2019).

Chalmers and Bustin (2007) analyzed the influence of degree of coalification and lithotypic composition of coal on CH₄ sorption. Their study was conducted on dull and bright samples separated from base coals. The results indicated a significant influence of maceral composition of high-rank coals on CH₄ sorption and its correspondence with content of vitrinite in coal. However, low-rank coals showed only slight differences in sorption capacity among dull and bright samples, and several dull samples showed higher sorption capacity compared to their bright equivalents (i.e., opposite tendency with respect to high-rank coals).

Radlinski and Mastalerz (2018) conducted measurements using the small-angle neutron scattering SANS/UNANS method to estimate porosity and pore size distribution from six samples of vitrinites with reflectance range of 0.55–1.28%. Their plots corresponding to pore sizes of 1–25 nm obtained for low-rank vitrinites were visibly different from those obtained for high-rank ones. The authors suggested that significant changes in the microstructure of vitrinite macerals occur with increase in degree of coalification.

This paper presents an analysis of the influence of petrographic composition of low-rank coal on the amount of gas accumulated in its porous structure and desorbed from it in coal-CO₂ and coal-CH₄ systems, with equalized influence of the degree of coalification of the research material. A series of low-pressure sorption experiments was carried out to achieve this goal. Isotherms of sorption and desorption of CO₂ and CH₄ were determined from three samples: base coal ($R_o = 0.51\%$) and two concentrates of lithotypes, vitrain and durain, isolated from the original sample. The scientific aim of the study was to describe theoretically the course of the investigated sorption processes. Selected sorption equations were used, namely Langmuir isotherm, Dubinin-Radushkevich isotherm and modified desorption model based on Langmuir equation, developed by Zhang and Liu (2017). The constants and parameters of these equations that were used for evaluation of the influence of petrographic composition of hard coal on the sorption of CO₂ and CH₄ include the following: maximum sorption capacity, a parameter reflecting adsorption energy, a parameter being a measure of hysteresis and reversibility of sorption and the areal hysteresis index.

RESEARCH MATERIAL AND EXPERIMENTAL METHODS

The original sample of coal was obtained from the “Sobieski” coal mine, located in the Upper Silesia Basin in Poland, from seam 207, located at a depth of 540 m. According to the international classification ECE-UN International In Seam Coal Classification (1998), this coal is medium-rank parabituminous D type coal. Before proceeding with the proper sorption measurements, it was necessary to prepare the test material. A decision was made to carry out a manual separation of, i.e., a part of the original coal sample (coal B) was crushed into lumps of about 5 mm. These small pieces of coal were separated by hand, in good light conditions, based on the appearance of individual fragments and split into concentrates of lithotypes, two of which were used in research: vitrain (coal V) and durain (coal D). From the pieces that corresponded to the appearance of clarain, a separate fraction was formed, though not analyzed in the presented studies. Next, the basic tests necessary to prepare the general characteristics of the coal were carried out.

However, their primary purpose was to verify the effectiveness of the separation process and to demonstrate the differences in the structure of individual samples. Proximate and ultimate analysis (only for original coal), petrographic composition analysis, vitrinite reflectance determination, real density determination and Fourier-transform infrared spectroscopy (FTIR) analysis were performed. The main part of the research was a series of sorption experiments carried out in the low-pressure range at 298 K on basic coal sample B, and samples of two concentrates of vitrain V and durain D; CO₂ and CH₄ were used as sorbates.

Ultimate analysis was carried out at the Central Mining Institute in Katowice. Moisture content of coal was determined according to the PN-80/G-04511 standard and ash content according to the PN-80/G-04512 standard. Oxygen content of coal was calculated as completion of elemental composition up to 100%, taking into account moisture and ash content (Table 1). Analyses of petrographic composition of coals and average vitrinite reflectance were carried out at the Faculty of Geology, Geophysics and Environmental Protection of the AGH University of Science and Technology in Krakow, Department of Deposit and Mining Geology, using AXIOPLAN mineralogical microscope and Axioplan-MPM-400 reflectometer by ZEISS OPTION (Table 2). The real density of the examined coals was measured with the helium method using automatic gas pycnometer AccuPyc™ 1330 (Table 2). The FTIR spectroscopy was performed with Frontier MIR/FIR Spectrometer in the wavelength range of 400–4000 cm⁻¹. The latter analyses were performed at the Faculty of Energy and Fuels of the AGH University of Science and Technology in Krakow.

Sorption experiments in low gas pressure range of 0–0.1 MPa (CO₂ and CH₄) in 298 K were carried out using ASAP 2010 micrometrics sorption apparatus (Fig. 1). The same equipment was also used to perform CO₂ sorption measurement in 273 K for the determination of specific surface area of micropores A_{mic} and micropores volume V_{mic} by the Dubinin-Radushkevich's method (Table 2). The device used the volumetric measurement technique. The dominant role of the upper part of the system is the distribution of gases and control of their flow. The lower part of the equipment includes measuring elements. Valve 6 separates both sections. Samples with grain sizes below 0.2 mm and weights of ~ 1.5 g were used for measurements. The test procedure included prior degassing of the measurement

Table 1. Specification of original coal B: proximate and ultimate analysis (Czerw et al. 2019)

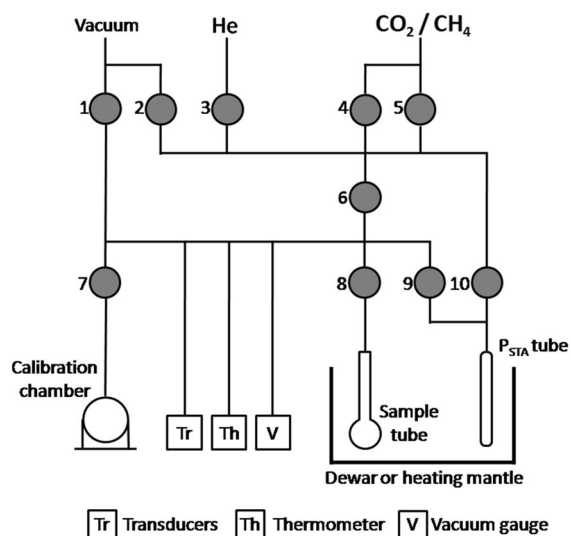
Parameter	Proximate analysis			Ultimate analysis				
	W ^a [%]	A ^a [%]	V ^a [%]	C ^a [%]	H ^a [%]	N ^a [%]	S ^a [%]	O ^a [%]
Original coal B	6.13	5.53	32.27	66.85	3.77	0.93	0.19	14.17

W: moisture content, A: ash content, V: volatile matter content, C, H, N, O, S: content of element C, H, N, O, S, respectively
^aAnalytical basis

Table 2. Specification of coal: maceral group composition, vitrinite reflectance, real density and micropore structure parameters (Czerw et al. 2019)

Parameter	Wi [%]	Li [%]	In [%]	Sm [%]	R ⁰ [%]	d _R [g/cm ³]	A _{mic} [m ² /g]	V _{mic} [cm ³ /g]
V	74.6	6	13.9	5.5	0.51	1.35	233.48	0.0936
B	51	11	36	2	0.51	1.40	183.04	0.0733
D	28.4	16.3	47.2	8.1	0.51	1.50	141.56	0.0567

Wi: vitrinite, Li: liptinite, In: inertinite, Sm: mineral matter, R⁰: vitrinite reflectance, d_R: real density, A_{mic}: specific surface area of micropores, V_{mic}: micropore volume

**Figure 1.** Schematic of sorption apparatus (ASAP 2010, Micrometrics) (Czerw et al. 2019).

and dosing space and the sample itself, in order to remove gases and vapors from its structure, including water. Before actual degassing, a sample was placed in a helium bath for 24 h to initiate the removal of adsorbed gases from coal surface. The degassing was carried out under vacuum, at temperature equal to the sorption measurement temperature, until the pressure increase over the sample was not higher than 2×10^{-1} Pa/min. The apparatus is capable of producing a vacuum of 10^{-3} Pa. The next step was to determine the dead volume of the

measurement space using helium. The heating mantle maintained a constant temperature of 298 K in the measuring system. Next, gas, CO₂ or CH₄ was introduced into the degassed measuring space until the system reached a constant pressure, i.e., the sorption equilibrium at a given pressure value, according to the used algorithm. The basic measurement cycle included a sequence of about 50 sorption and desorption stages per sample.

SORPTION MODELS

To describe the theoretical course of the investigated sorption processes, two sorption isothermal equations—the Langmuir isothermal equation and the Dubinin–Radushkevich isothermal equation—and a modified desorption model based on the Langmuir equation developed by Zhang and Liu (2017) were used.

The Dubinin–Radushkevich equation is a model widely used for microporous sorbents, and it is seen as representative of systems in which adsorption occurs (Dubinin and Radushkevich 1947; Kapoor et al. 1989; Zhao et al. 2016). It is a traditional model that treats coal as a rigid structure that does not change as a result of interaction with CH₄ and CO₂ (Wang et al. 2014). Therefore, its application in the case of coal requires the assumption that we are not dealing with a sorbent of flexible structure that does not change because of interaction with the sorbed medium. There are several forms of

the Dubinin–Radushkevich isothermal equation. The variant used here was:

$$V = V_0 \exp \left[- \left(\frac{RT}{\beta E} \ln \frac{p_0}{p} \right)^2 \right] \quad (1)$$

where V is volume (cm^3 STP/g) adsorbed at relative pressure of p/p_0 at temperature T , p_0 is CO_2 saturated vapor pressure (Pa) at temperature T , V_0 is maximum volume (cm^3 STP/g) of adsorbed gas, E is energy (J/mol) of adsorption, β is the affinity coefficient (unitless) of the adsorbate, R is the universal gas constant (8.3145 J/mol K) and T is the equilibrium temperature (K) of gas adsorption. The variant of the Dubinin–Radushkevich equation used here is based on Polanyi's potential theory of adsorption and is adequate for adsorption of vapors on porous adsorbents in a wide range of pressure. It contains only two parameters: V_0 and βE (Dubinin and Radushkevich 1947; Kapoor et al. 1989).

The apparent limitation of the area of application of the Dubinin–Radushkevich equation is the necessity of occurrence of adsorbate in the state of vapor and the possibility of giving the value of saturated vapor pressure p_0 . Under experimental conditions, the critical temperature of CO_2 (304.18 K) is not exceeded, while CH_4 at 298 K is in a gaseous state. Therefore, the missing parameter was determined using the reduced Kirchhoff equation (Reich et al. 1980; Li and Gu 2004; Machnikowski and Sciazko 2010). The formula allows calculating the saturated steam pressure analogue at temperatures above critical temperature by extrapolating the Kirchhoff equation; thus,

$$p_s = p_c \exp \left[h \left(1 - \frac{T}{T_c} \right) \right] \quad (2)$$

$$\text{where } h = \frac{T_{\text{nbp}}}{T_c} \cdot \frac{\ln p_c}{1 - \frac{T_{\text{nbp}}}{T_c}} \quad (3)$$

and p_s is the saturated vapor pressure analogue (Pa) at temperature T , p_c is the critical pressure (Pa), T is the system temperature (K) at equilibrium, T_c is the critical temperature (K) of the gas and T_{nbp} is the boiling point (K) at normal pressure.

The Langmuir adsorption model presents the adsorption process as a phenomenon consisting of interaction of individual adsorbate molecules with adsorbing sites on the homogenous adsorbent surface, resulting in the formation of a monomolecular adsorbate layer in dynamic equilibrium with the

surrounding medium (Langmuir 1918). The equation is widely used because of its simplicity, effectiveness in matching experimental data and rational explanation of its characteristic parameters. It is also used to describe the course of sorption on coal. There are several forms of the Langmuir isothermal equation. The one used here was chosen to describe experimental data in order to determine the constant values of the equation for individual coal–gas systems; thus,

$$V = V_m \frac{K \cdot p}{1 + K \cdot p} \quad (4)$$

where V is volume (cm^3 STP/g) of gas adsorbed at equilibrium pressure p and temperature T , V_m is the maximum adsorbed capacity, an equivalent of the volume (cm^3 STP/g) of sorbent monolayer, K is the constant of adsorption equilibrium (unitless) also referred to as Langmuir's constant and p is the equilibrium pressure (Pa) of gas at temperature T . In order to obtain constants of Langmuir equation, which allow calculating the surface hysteresis index (AHI), an alternative form of sorption equation and a modified desorption equation based on Langmuir equation (Zhang and Liu 2017) were used here; thus,

$$V = V_{La} \frac{p}{p_L + p} \quad (5)$$

$$V = V_{Ld} \frac{p}{b \cdot p_L + p} \quad (6)$$

where V is the absolute volume (cm^3 STP/g) of gas adsorbed under pressure p at temperature T , V_{La} and V_{Ld} are the constants corresponding to the maximum absolute adsorption capacity (cm^3 STP/g) of the sorption and desorption system, respectively, p is the gas equilibrium pressure (Pa) at temperature T , p_L is the gas equilibrium pressure (Pa) when $V = \frac{1}{2}V_{La}$ at temperature T , b is the hysteresis parameter (unitless) representing the difference in desorption rate relative to adsorption and expressing what fraction of the surface area of the adsorbent filled at the adsorption stage is the surface capable of releasing gas during desorption.

The AHI is one of the indices that express the degree to which the sorption process differs from the corresponding desorption. It is equivalent to the surface increment under the desorption curve A_{de} relative to the surface under the sorption curve A_{ad} , expressed as a percentage of the surface under the sorption curve; thus,

$$\text{AHI} = \frac{A_{de} - A_{ad}}{A_{ad}} \cdot 100\% \quad (7)$$

Values of A_{de} and A_{ad} are obtained by integrating Eqs. 5 and 6 over the entire pressure range, i.e., from zero to the final pressure of the equilibrium pressure p_f . By transforming these equations, combining them with Eq. 7 and expressing the ratio of final sorption pressure p_f and Langmuir pressure p_L in the form of parameter p_r ($p_r = p_f/p_L$), the following formula was obtained (Zhang and Liu 2017):

$$\text{AHI} = \frac{(b + p_r)[p_r - b \cdot \ln(1 + \frac{p_r}{b})] - (1 + p_r)[p_r - \ln(1 + p_r)]}{(1 + p_r)[p_r - \ln(1 + p_r)]} \cdot 100\% \quad (8)$$

RESULTS AND DISCUSSION

The maceral composition of the original coal and the isolated concentrates of the lithotypes confirm the acceptable accuracy of the manual separation process (Table 2). The amount of vitrinite group macerals is higher by 23.6% in coal V and lower by 22.6% in coal D compared to coal B. For inertinite group macerals, an increase of 11.2% for sample D and a decrease of 22.1% for sample V were observed. In the opinion of the authors, the separation process was effective and sufficient for the purpose of the developed series of experiments.

The values of A_{mic} and V_{mic} determined using the Dubinin–Radushkevich method (Table 2) are the highest for coal V and the lowest for coal D. This indicates that these parameters increase with increase in the content of vitrinite group macerals in coal. The results obtained for the tested coals V, B and D are generally comparable to those obtained by Chalmers and Bustin (2007) for samples F82 dull and bright (R_o 0.5%, vitrinite content 47.6% and 89.2%, respectively). However, they are higher than values for other coals of similar rank and petrographic composition obtained by Mastalerz et al. (2008) (samples 2005-787-2 and 2005-787-4), Zhao et al. (2016) (TN sample) and Teng et al. (2017) (clarain and durain samples close in terms of composition to coals V and B).

The structure of coal is bimodal. Aromatic and hydro-aromatic macromolecules cross-linked with covalent, hydrogen and van der Waals bonds form a chained three-dimensional network in which there are molecules of lower molar mass trapped in or bound to pores. The results of FTIR spectroscopy

provided information on the structure of coal in terms of carbon and hydrogen groups and oxygen groups, enabling the assessment of differences in the structure and character of sample surfaces. In general, the FTIR spectra obtained for coals V, B and D are similar (Fig. 2). For all the coals, a strong absorbance is observed at wavelength of 3422 cm^{-1} (Zhang et al. 2015), which corresponds to the broad stretching region of O–H bond and indicates the presence of hydroxyl groups forming hydrogen bonds. Coal V is characterized by the highest intensity at this wavelength, and the presence of these groups has a significant influence on the adsorption of polar sorbates. Notable peaks are lacking in the obtained FTIR spectra corresponding to stretching region of C–H bond of aromatic character (i.e., at 3030 cm^{-1}), whereas those corresponding to C–H bonds of aliphatic character (Teng et al. 2017) are marked at $2800\text{--}3000 \text{ cm}^{-1}$, but in case of coal V a distinct peak occurs only at 2930 cm^{-1} . Absorption peaks corresponding to wavelength of 1610 cm^{-1} (Ibarra et al. 1996), which indicate conjugated C=C structures, occur with significantly higher intensity and narrower region in the case of vitrinite-rich coal V in comparison with coal B. Strong absorbance in the aromatic carbon region ($1550\text{--}1650 \text{ cm}^{-1}$) occurs due to stretching of the double bond C=C. In the aliphatic bending region ($1350\text{--}1450 \text{ cm}^{-1}$), which corresponds to the deformations of the $-\text{CH}_2-$ and $-\text{CH}_3$ bonds (Teng et al.

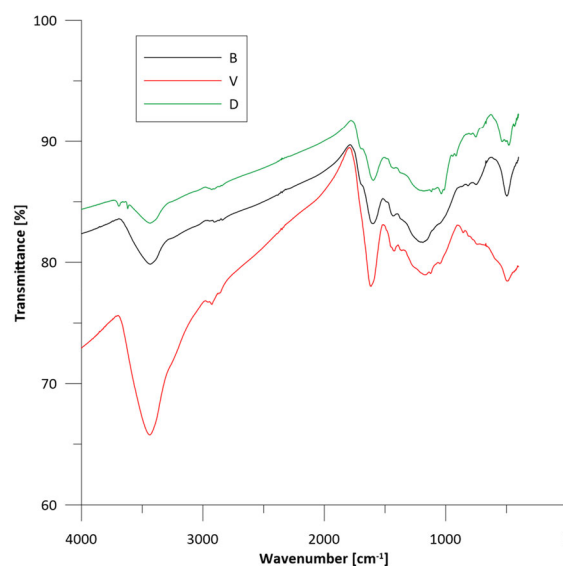


Figure 2. FTIR spectra of coal samples under investigation: B, V and D (Czerw et al. 2019).

2017), peaks (at 1430 cm^{-1}) are noticeable and increase from coal D, through coal B, to coal V. Conversely, in the aromatic out-of-plane bending region representing C–H bonds ($700\text{--}900\text{ cm}^{-1}$) (Teng et al. 2017) the intensity of peaks (750 cm^{-1}) is weak and decreases from coal D, through coal B, to coal V. In case of coal D, peaks at wavelength 1030 cm^{-1} were registered, most probably corresponding to the presence of a mineral matter (Zhang et al. 2015).

The sorption capacity of sample V toward CO_2 obtained at the end of the sorption part of the experiment is higher ($19.73\text{ cm}^3/\text{g}$) compared to the inertinite-rich sample D ($12.60\text{ cm}^3/\text{g}$), whereas sample B has an intermediate value ($16.08\text{ cm}^3/\text{g}$) (Fig. 3a). This tendency is consistent in the whole range of tested pressures and indicates indirectly the relationship between maceral composition and sorption properties of the low-rank coal– CO_2 system. Individual lithotypes of coal differ in terms of structure at the molecular level as well as porosity and pore volume distribution, surface character and, thus, sorption properties in relation to CO_2 . The composition of durain is dominated by inertinite and liptinite; hence, it is characterized by a higher share of meso-pores and a lower share of micropores compared to vitrain with the same degree of coalification, and consisting mostly of vitrinite (Chalmers and Bustin 2007). The values of sorption capacity obtained for the tested samples V, B and D are comparable to those obtained by Teng et al. (2017) for clarain and durain samples of comparable rank and composition and by Zhao et al. (2016) for their TN sample. The results of the desorption part of this study also indicate positive correlation between the share of vitrinite group macerals, and the size of the hysteresis loop revealed during this stage of the experiment. Not all hysteresis loops are closed in case of this gas as sample V retained part of the gas in its structure (Fig. 4a).

The results of the sorption experiments for CH_4 revealed that the isothermal course is very close for samples V and D, whereas the isothermal course for sample B is above these curves (Fig. 3b). The maximum values obtained were $2.53\text{ cm}^3/\text{g}$, $2.57\text{ cm}^3/\text{g}$ and $3.16\text{ cm}^3/\text{g}$ for V, D and B samples, respectively. The isotherms of CH_4 sorption are linear. The sorption capacity of the coals under investigation in relation to CH_4 increases proportionally with increase in the equilibrium pressure of sorption. In contrast, desorption isotherms differ from this tendency and are closer to a typical curve shape

(Fig. 4b). The isotherms of CH_4 desorption show hysteresis, the size of which is consistent with the trend observed in the case of CO_2 desorption; however, all hysteresis loops for this gas are closed.

Several potential causes of occurrence, and shape of the sorption hysteresis curve can be indicated (Wang et al. 2014). The presence of residual moisture, deformation of coal structure/swelling and occurrence of capillary condensation are plausible factors whose influence should be rejected due to the pressure conditions of this experiment. Experimental inaccuracies may be assumed to occur, such as inappropriate waiting time for the sorption balance. Considering this topic, it is worthwhile to pay attention to the aspect of the type of gas interactions with coal. Weishauptová et al. (2004) put it as follows: If desorption is measured simultaneously, it shows unambiguously that sorption is not reversible as required for pure adsorption in micropores, which indicates a side interaction. By means of the desorption branch of the isotherm, based on certain assumptions, the combined isotherm can be analyzed, and thus, the adsorbed and absorbed parts distinguished quantitatively. Weishauptová et al. (2004) measured adsorption and desorption branches of the CH_4 isotherm at 298 K, within the pressure range 0–1 bar. In their study, two samples of bituminous coals A (Rr 1.48%) and B (Rr 0.88%) from the Upper Silesian coal basin and brown coal C (Rr 0.26%) from the North Bohemian basin were used. The results were as follows. The adsorption/desorption process is not reversible, whereas the desorption branch lies markedly over the adsorption one within the whole pressure range. The position of the desorption branch reflects the release of smaller gas amount compared to the total amount sorbed. The amount of gas left bound in the sorbent can be considered as the absorbed part, because according to the assumed binding mode the rate of release of the absorbed gas may be lower at several orders than the gas adsorbed. Inability to evacuate the residual CO_2 from sample V, 19% of obtained maximal sorption capacity, may follow the same mechanism mentioned above.

Two sorption equations, namely Dubinin–Radushkevich equation and Langmuir equation, were used to describe the theoretical results of the research. These equations showed very good agreement with the experimental data (Fig. 3). However, in the case of coal– CO_2 systems, better effects were obtained using the Dubinin–Radushkevich equation. In relation to coal– CH_4 systems, differences in the

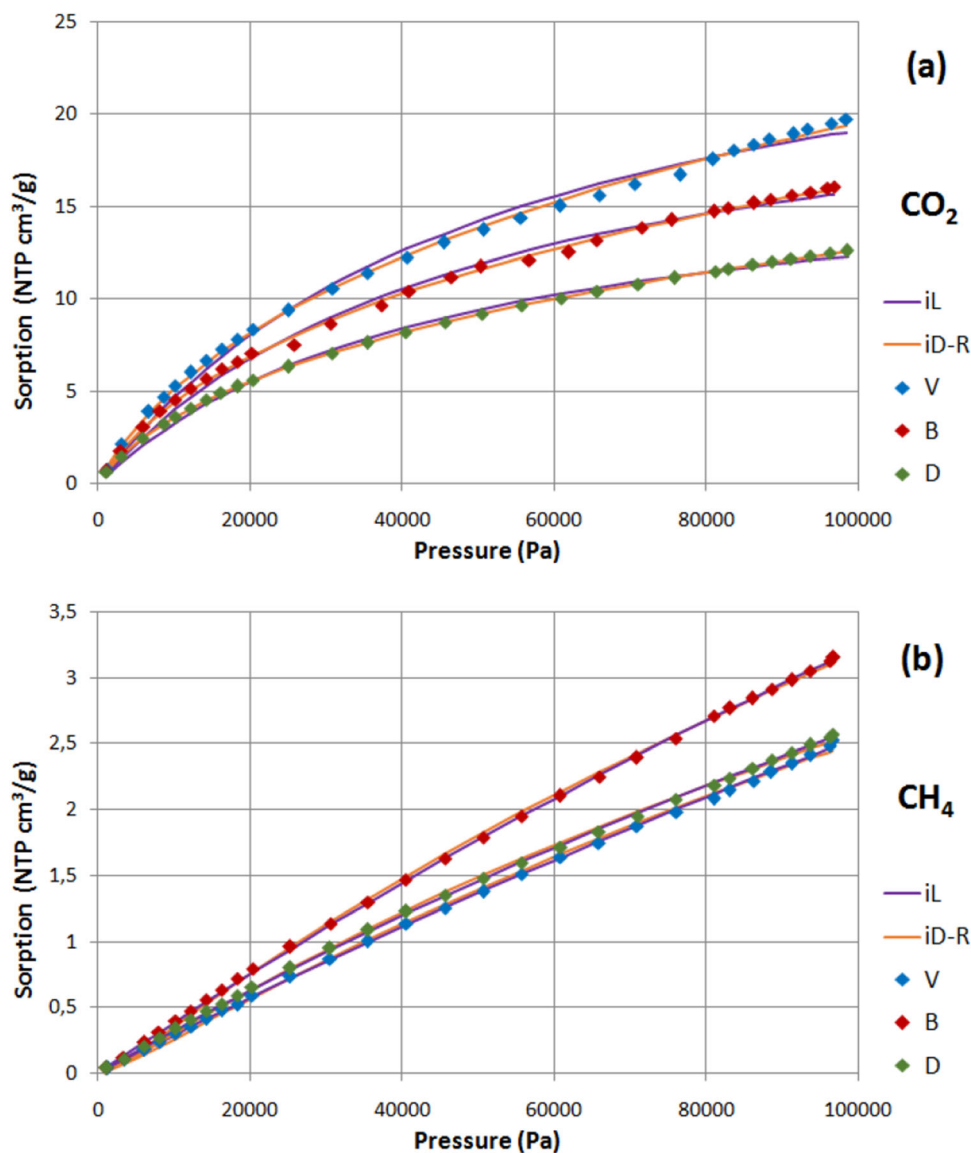


Figure 3. Low-pressure sorption isotherms of coal samples B, V and D for gases: **a** CO₂ and **b** CH₄. (iL = Langmuir equation fit; iD-R = Dubinin–Radushkevich equation fit).

quality of the fit are minimal and indicate a slight advantage of the Langmuir equation.

The relation of Dubinin–Radushkevich equation parameters corresponding to the maximum adsorption capacity V_0 of coal for individual samples was consistent with the relation of their capacities highest values obtained in the sorption studies (Table 3). In turn, the βE parameter related to free adsorption energy maintains almost identical value for a given gas in three tested systems, with negligible increase in value in the order of coal V < coal

B < coal D. For the coal–CO₂ system, the differences were about 1–2% and for coal–CH₄ systems, about 1–1.5%. The values of these parameters for particular gases, CO₂ and CH₄, are comparable to each other as 4:3. On this basis, it can be concluded that the maceral composition of the examined samples does not affect the mechanism of sorption of individual gases and does not differ between macerals of inertinite and vitrinite groups (Baran et al. 2018a, b; Czerw et al. 2019). It should be noted that the pressure range of the experiments was 0–

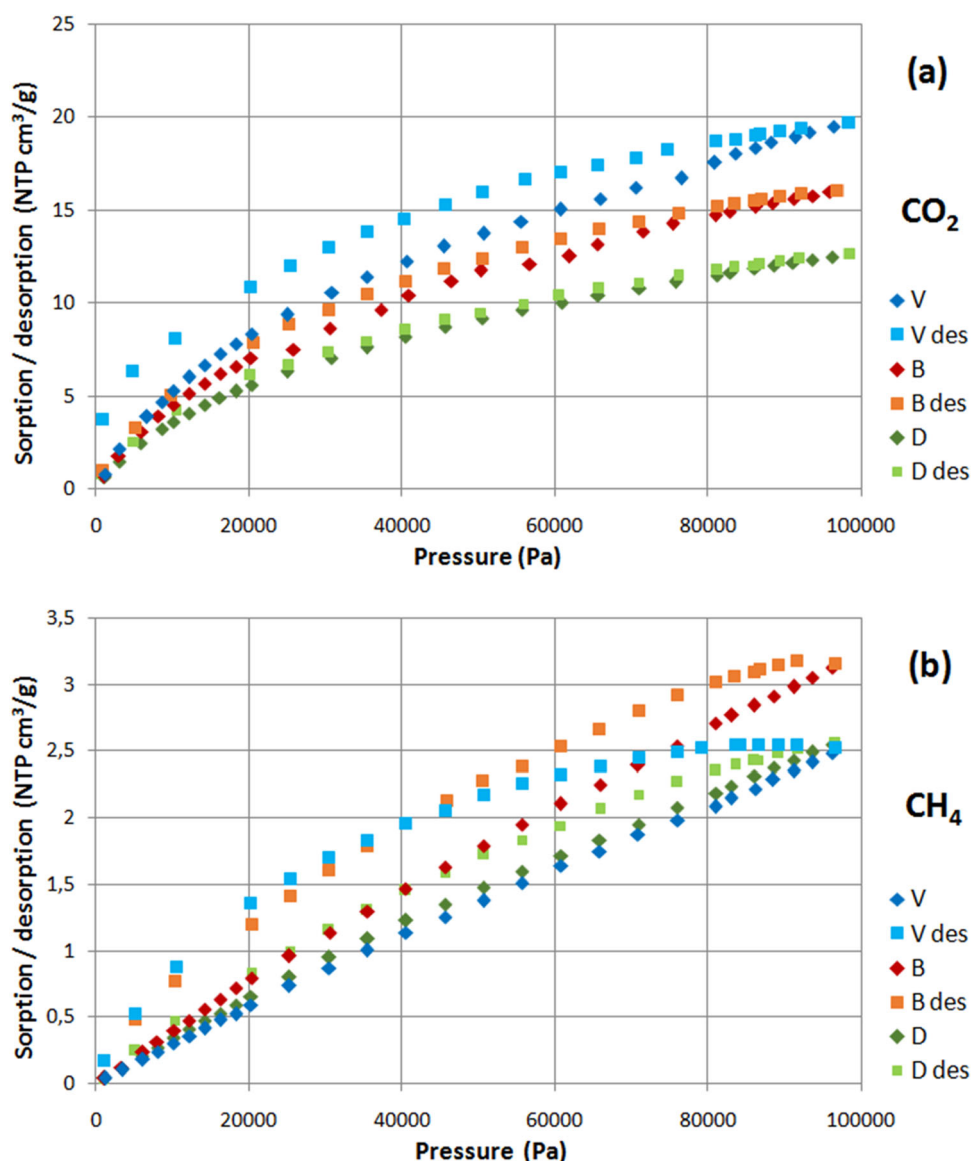


Figure 4. Low-pressure sorption and desorption isotherms of coal samples B, V and D for gases: **a** CO₂ (Czerw et al. 2019) and **b** CH₄.

0.1 MPa. Maximum equilibrium pressures were 98.5 kPa for CO₂ (except sample B) and 96.7 kPa for CH₄. These correspond to relative pressures p/p_0 of 1.53% and 0.95%, respectively, with the assumed adequate p_0 of 6.434 MPa and 10.143 MPa (calculated from the reduced Kirchhoff equation).

The ratio of Langmuir equation parameters corresponding to the maximum capacity of the monolayer of CO₂ for individual samples was consistent with the ratio of their highest values obtained in the sorption experiments (Table 3). However, in

case of CH₄, a distinct value of V_m parameter for coal V was noted. It results from the fact that the basis for calculations of equation constants was the obtained data corresponding to the initial straight-lined parts of the isotherm, but not the data from the broader pressure range in which the curve deflection occurs, as in the case of data obtained for CO₂. Extrapolation of calculated CH₄ sorption isotherms according to Langmuir model to higher pressures revealed that the curve corresponding to sample V is increasing with higher slope than that obtained for

Table 3. Model fitted parameters for sorption and desorption and areal hysteresis index for systems under investigation (¹Czerw et al. 2019)

Parameter	V_0 [cm ³ /g]	βE [J/mol]	V_m [cm ³ /g]	K	p_L [kPa]	b	AHI [%]
Carbon dioxide CO ₂							
V	50.38 ¹	10581 ¹	29.26	0.00252	52.9	0.423	13.15
B	40.90 ¹	10701 ¹	23.76	0.00267	50.0	0.769	3.92
D	30.89 ¹	10897 ¹	17.89	0.00296	44.9	0.889	1.73
Methane CH ₄							
V	15.58	8474	18.75	0.00021	624.4	0.050	37.495
B	18.59	8618	18.00	0.000291	430.4	0.193	17.288
D	14.48	8722	12.60	0.000349	357.2	0.355	9.9495

V_0 : maximum volume of adsorbed gas, βE : free energy of adsorption, V_m : volume of the monolayer, K : equilibrium constant, p_L : gas equilibrium pressure at ($V = \frac{1}{2}V_{L0}$), b : hysteresis parameter, AHI: areal hysteresis index

sample B and at the pressure of about 2 MPa the two isotherms cross. This situation does not occur in the case of extrapolation of isotherms based on the Dubinin–Radushkevich model. However, among adsorption equilibrium constants K , an increase in this parameter values in the order of coal V < coal B < coal D coals was observed (Table 3). For coal–CO₂ systems, relative differences in the value of parameters are smaller than for coal–CH₄ systems. The values of these parameters for CO₂ are 8–9 times higher than for CH₄. On this basis, it can be concluded that maceral composition of the examined samples affects the dynamics of sorption of single gases and differs between macerals of inertinite and vitrinite groups.

The Langmuir equation and a modified desorption model based on the Langmuir equation, developed by Zhang and Liu (2017), and the AHI (Table 3), were used to evaluate the course of sorption and desorption processes. The values of AHI calculated for individual gases CO₂ and CH₄ accurately capture the differences in the course of curves corresponding to the accumulation of sorbent in the structure of coal and the stage of its evacuation. Values of b parameters calculated for coal–CO₂ systems were correct (Table 3). The open hysteresis loop of coal V was reflected in a significantly lower value of b in comparison with coal B and coal D. However, in the case of coal–CH₄ systems, the obtained values of b parameters were incorrect. An error resulted, again, from the specificity of isotherm input data constituting the points of the curve corresponding to its initial straight-line part. Hence, the values of equilibrium pressure CH₄ corresponding to half of the maximum adsorption capacity p_L were far beyond the experimental pressure range.

CONCLUSIONS

The following conclusions can be drawn from this study:

- The sorption capacity of low-rank coal in relation to CO₂ and the size of hysteresis loop are related to its petrographic composition.
- No correlation was observed between the sorption capacity of the research material and CH₄ by its petrographic composition. Isotherms of methane desorption show hysteresis, the size of which correlates with its petrographic composition.
- The βE parameters corresponding to free energy of adsorption in the Dubinin–Radushkevich equation reached the same values for all CO₂ systems and all CH₄ systems, indicating lack of influence of maceral composition on the sorption mechanism in case of particular gases.
- The sorption equilibrium constant K in the Langmuir equation increases with decrease in vitrinite content in coal, indicating that maceral composition influences the dynamics of CO₂ and CH₄ sorption.
- The AHI and hysteresis parameter b provide a good tool to evaluate the difference in the course of sorption and desorption isotherms.
- The Dubinin–Radushkevich and Langmuir equations show very good agreement with the experimental data. It should be stressed that the issues discussed concerning experimental data cover only the beginning of the isotherm, up to 100 kPa. The authors favor using the Dubinin–Radushkevich isotherm rather than the Langmuir equations in such cases.

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CONFLICT OF INTEREST The authors declare that they have no conflict of interest.

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