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Multi-Parameter Analysis of Gas Losses Occurring during the Determination of Methane-Bearing Capacity in Hard Coal Beds

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Abstract: The content of natural methane in hard coal seams, called methane-bearing capacity, is the basic parameter that enables the level of methane hazard to be determined in hard coal mines. This parameter is also used to determine the potential quantities of methane that can be collected and used for energy purposes and the amount of its harmful emission to the atmosphere. Direct methods are most often used to determine methane-bearing capacity. An important aspect that has a great influence on the final result of the research is the gas losses generated at the stage of sampling. Under the conditions of the Polish mining industry, the direct drill cuttings method is used to determine the methane-bearing capacity. Gas losses are compensated for in this method with the use of the coefficient 1.12, by which the obtained result is multiplied. In this paper, a multi-parameter analysis of gas loss in the determination of methane-bearing capacity in hard coal seams has been carried out. Several experiments were performed to identify the most important aspects to be taken into account to obtain a correct result. A methane-bearing capacity test was conducted using two direct methods: the direct drill cuttings method, otherwise known as the single-phase vacuum degassing method, and a method based on the United States Bureau of Mines standards. Sorption studies, such as methane sorption kinetics tests, were also conducted in which sorption properties, such as sorption capacity, effective diffusion coefficient, and half sorption time, were determined. Methane sorption isotherms were also determined, and pore structure was analysed. Based on the obtained test results, an analysis was carried out which made it possible to present appropriate conclusions concerning the gas losses during the methane-bearing capacity test, generated at the stage of sampling. The final result of the work was the proposal of a new gas loss coefficient for the direct drill cuttings method of methane-bearing capacity determination.

Keywords: methane; hard coal; methane hazard; lost gas; methane-bearing capacity

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1. Introduction

Methane is a natural gas accumulated in hard coal beds and occurs in two different forms [1,2]. It can occur in a sorbed form, i.e., deposited in pores, or as free gas in macropores, cracks, and fissures [3–5]. Methane in hard coal beds, and the related methane hazard, is one of the most dangerous natural hazards associated with hard coal mining [6–11]. Despite the significant progress in identifying and combating the methane hazard, its increase is observed in many mining areas, which is associated with increasing the depth of mining, increasing methane-bearing capacity, and coal bed gas pressure [8]. Proper identification of this hazard is very important in terms of the safety of mining works. The analysis of phenomena related to gas transport in a coal structure, apart from the aspect of work safety in mining, is very important in the context of using coal bed methane for energy purposes (CBM, CMM, AMM) and reducing its harmful emission to the atmosphere. Methane is the main component of coal bed methane (CBM) gas accumulation in coal seams and tight gas accumulation in silt-sand formations, occurring between the coal seams [12]. Unconventional gas sources, such as coal bed methane, have become a growing

global interest with great potential [4,13,14]. The content of natural methane in coal beds, so-called methane-bearing capacity, is the basic parameter that allows experts to determine the potential quantities of methane which can be collected and used for energy purposes and to determine the size of its harmful emission to the atmosphere. Methane-bearing capacity is defined as a measure of the natural methane content of coal per mass unit (Mg) of dry, ash-free coal determined in the unit of m^3 CH_4/t_{daf} [15].

An important aspect to consider when discussing the above-mentioned issue is the extensive coal pore system. All types of pores are present: macropores with a diameter >50 nm, mesopores 50–2 nm, and the smallest micropores <2 nm [16]. Almost the entire pore volume is accounted for by micro- and submicropores, which are the primary sorption system of hard coals [17–19]. Mesopores and macropores act as transport pores and are responsible for the diffusion and movement of sorbed molecules into the micropore structure [20,21]. As the degree of metamorphism of coals increases, the proportion of microporosity increases at the expense of meso- and macroporosity.

Over the years, various methods have been described in the literature, both direct and indirect, for the determination of natural methane content in hard coal and shale [22–34]. A very important aspect that has a great influence on the final result of the methane-bearing capacity determination is the gas loss generated while taking a sample for testing. These gas losses are generated from the time a coal sample is taken, i.e., the start of drilling, until it is placed in a hermetically sealed container. In the conditions of the Polish mining industry, the recognition of coal seams for the content of natural methane in coal (methane-bearing capacity) is based on the Polish standard PN-G-44200:2013-10 [35], describing the determination of methane-bearing capacity using the direct drill cuttings method. In this method, gas losses are compensated for by a constant factor of 1.12. Hard coal, due to its extensive pore structure, is a heterogeneous material in which sorption processes occur with different dynamics [36–38], and therefore it is very difficult to determine one universal coefficient correcting the final determination result.

In this paper, a multi-parameter analysis of gas loss during methane-bearing capacity determination is carried out based on a series of tests and the mutual correlation of the obtained results. The methane-bearing capacity tests were conducted using two direct methods: the direct drill cuttings method, otherwise known as the single-phase vacuum degassing method, and the United States Bureau of Mines method. The USBM method allows the determination of the gas components: lost gas, desorbing gas, and residual gas. Therefore, it is possible to determine individual gas losses for each of the analysed coal samples and to compare the results with those obtained by the direct drill cuttings method. The above analysis will be extended to the interpretation of the obtained sorption test results. Among them, methane sorption kinetics studies were performed, resulting in the determination of sorption parameters, such as effective diffusion coefficient, sorption capacity, half sorption time, and the determination of methane sorption isotherms based on the Langmuir model. Additionally, porous structure studies were performed along with the determination of micro-, meso-, and macropore volumes and surfaces according to the Brunauer-Emmett-Teller and Dubinin-Radushkevich models. The results of this work can be used to develop new, or improve current, solutions for estimating the amount of gas lost during coal sampling for methane-bearing capacity determination.

All abbreviations used in this article are explained in the form of Table 1.

Table 1. Table of abbreviations.

Abbreviation	Explanation	Abbreviation	Explanation
USBM	United States Bureau of Mines	D-R	Dubinin-Radushkevich model
CBM	Coal bed methane	BJH	Barrett-Joyner-Halenda model
CMM	Coal mine methane	USCB	Upper Silesian Coal Basin
AMM	Abandoned mine methane	A	Ash content
M_o	Methane-bearing capacity	W_h	Hygroscopic moisture
daf	Dry, ash-free	W_{ex}	Transient moisture
D_e	Effective diffusion coefficient	V^{daf}	Volatile matter content
a_{daf}	Sorption capacity	Q_L	Lost gas
$t_{1/2}$	Half sorption time	Q_D	Desorbing gas
BET	Brunauer-Emmett-Teller model	Q_R	Residual gas

2. Materials and Methods

2.1. Study Area

Multi-parameter analysis of gas losses during methane-bearing capacity determination was conducted based on coal samples collected in Poland from mines located in the Upper Silesian Coal Basin. The Upper Silesian Coal Basin is one of the largest coal basins in Europe with a total area of 7500 km^2, of which 5600 km^2 are in Poland. The other 1900 km^2 belong to the Czech Republic [39,40]. Currently, 79.99% of the documented balance resources of Polish hard coal are located in this basin [35]. Detailed information on the geological structure is presented in the literature [36,37]. Figure 1 presents the location of the Upper Silesian Coal Basin [41–43]. One of the basic problems of many USCB mines is their high methane content. A large number of these mines have highly methane conditions and, for operational safety reasons, must carry out methane drainage [40,44,45]. These are the reasons why research into the proper determination of methane-bearing capacity is very important.

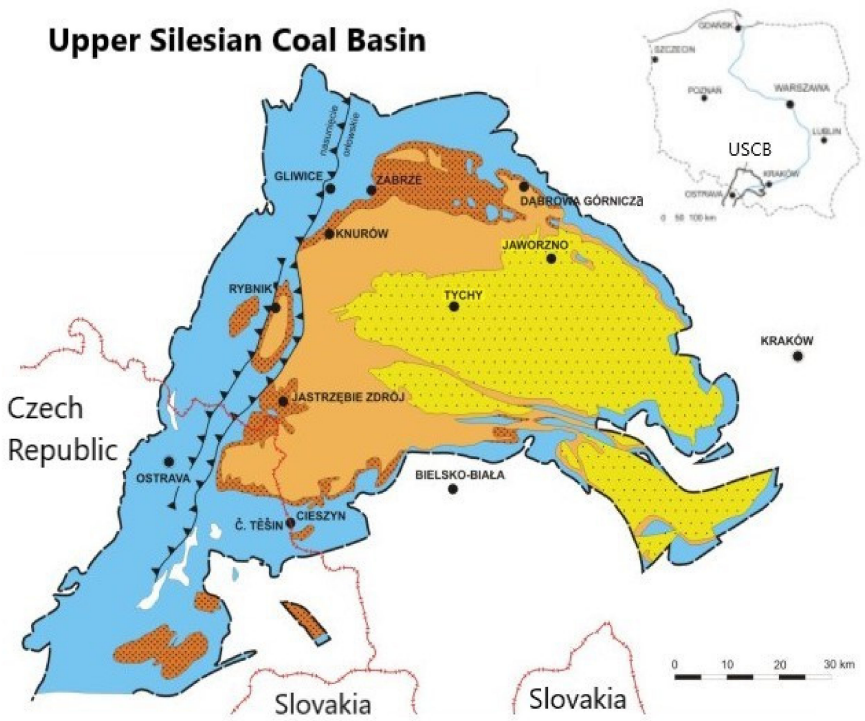

Figure 1. Location of the Upper Silesian Coal Basin study area [41–43] (modified).

For the purposes of this article, several tests were carried out based on coal samples taken from 9 mines located in the Polish part of the Upper Silesian Coal Basin. In order to preserve the confidentiality of the Polish mines and the obtained test results, the samples were marked as P-1–P-9. The mines from which the samples were taken were selected in such a way that the results of methane-bearing capacity were diverse within the determined

range. For methane-bearing capacity testing, coal samples were taken from active longwalls that were in operation at least 24 h before the scheduled sampling. For the USBM method, the core samples were taken from the depth of 2.0–2.5 m, while for the direct drill cuttings method, samples from drilling a borehole at a depth of 3.5–4.0 m were collected. For the remaining sorption tests, drill cuttings samples were collected from the depth of 2.0–4.0 m and then prepared according to the required test procedure. The description of the test procedures for each analysis is presented in the following sections of the paper. The specifics of the coal samples collected for testing are described in Table 2.

Table 2. Coal samples taken from the Upper Silesian Coal Basin intended for laboratory testing.

Sample Name	Methane-Bearing Capacity		Sorption Tests		
	Single-Phase Vacuum Degassing	**USBM**	**Sorption Kinetics**	**Sorption Isotherms**	**Structure Analysis**
P-1 P-2 P-3 P-4 P-5 P-6 P-7 P-8 P-9	Core samples Length~30 cm Sampling depth 2.0–2.5 m	Drill cuttings Weight~100 g Sampling depth 3.5–4.0 m	Drill cuttings Weight~1 kg Sampling depth 2.0–4.0 m	Drill cuttings Weight~1 kg Sampling depth 2.0–4.0 m	Drill cuttings Weight~1 kg Sampling depth 2.0–4.0 m

2.2. Direct Drill Cuttings Method for Methane-Bearing Capacity Determination—Single-Phase Vacuum Degassing

The basic method of methane-bearing capacity determination currently applied in the Polish mining industry is the direct drill cuttings method, otherwise known as the single-phase vacuum degassing method. It is based on the requirements of the Polish standard PN-G-44200:2013-10 [29] and the Regulation of the Minister of Energy of 23rd November 2016 on the detailed requirements for the operation of underground mining plants [46]. The presented method is based on testing drill cuttings samples taken from a drilling depth of 3.5–4.0 m into specially closed hermetic containers (Figure 2), with steel balls inside. In the first step of the study, the sample is crushed using steel balls inside a container on a mechanical shaker. Single-phase vacuum degassing of the coal is then conducted, and the resulting gas is analysed by gas chromatography to determine the percentage of methane in the gas mixture. The remaining coal sample is then subjected to physicochemical analysis, which determines the ash content, hygroscopic moisture, transient moisture, and volatile matter content. The above parameters are necessary to present the final result in terms of dry, ash-free substances. The result is then converted to compensate for gas losses. For this purpose, the coefficient 1.12 is used, taking into account the 12% loss, which is included in Equation (1) [34,35].

$$M_o = 1.12 \times M_L \quad (1)$$

where M_o is the methane-bearing capacity taking into account gas losses (m^3 CH_4/t_{daf}), and M_L is the methane-bearing capacity determined in the laboratory, without gas losses (m^3 CH_4/t_{daf}).

Figure 2. Hermetically sealed containers for coal sampling.

2.3. United States Bureau of Mines Direct Method for Methane-Bearing Capacity Determination

The second method described in this paper, for determining methane-bearing capacity, is based on the United States Bureau of Mines standards. This method has been described by many researchers in the literature, proposing various possibilities of applying this method as well as its modifications [11,26,28,29,31,47,48]. It is used for identifying and documenting coal bed methane deposits. This method involves observing the free degassing of the coal core and measuring the volume of desorbing gas at atmospheric pressure. With the USBM method, it is possible to determine the individual gas components, such as lost gas, desorbing gas, and residual gas (Equation (2)). This allows individual gas losses to be determined and taken into account when determining the final methane-bearing capacity value for each coal sample analysed.

$$Q_T = Q_L + Q_D + Q_R \quad (2)$$

USBM desorption tests are performed based on the American Society for Testing and Materials (ASTM) standard ASTM D7569/D7569M-10 [44] and the United States Department of the Interior documentation RI 7767 [28]. The basis for testing by this method are core samples of approximately 30 cm in length and 48 or 62 mm in diameter taken into specially constructed hermetic containers with pressure and temperature sensors (Figure 3a). In the originally described USBM method, which was developed from the Bertard method [29] and described in ASTM D7569/D7569M [49], the measurement is made by reading the amount of liquid displaced by the desorbing gas in an inverted measuring cylinder. At the Central Mining Institute, USBM tests are conducted on a specially constructed test stand (Figure 3b). It contains a system of cylinders and volumetric flasks connected to hermetic containers located in a water bath that maintains a constant process temperature. Conditions such as temperature and pressure in the container are controlled and continuously recorded by an integrated system of computer-controlled sensors. At the time of measuring the volume of desorbing gas from the coal core, the analysis of its composition based on the gas chromatography method is performed at set intervals.

The volume of the desorbing gas is observed until its desorption from the sample has completely ceased. In the next step, the volume of residual gas is measured. For this purpose, a piece of core after free degassing is placed in a hermetically sealed container with steel balls and subjected to crushing. The volume of gas released is then measured and its composition analysed by gas chromatography. The last step involves determining the volume of gas lost, which is graphically derived from the desorption plot obtained from the acquired data. The desorption curve is extrapolated until it intersects with the ordinate axis. The intersection of the desorption curve with the ordinate axis gives the value corresponding to the residual gas (Figure 4).

(**a**) (**b**)

Figure 3. Central Mining Institute test stand for methane-bearing capacity identification by the USBM direct method: (**a**) Hermetically sealed steel containers with pressure and temperature sensors; (**b**) Central Mining Institute USBM dedicated test stand.

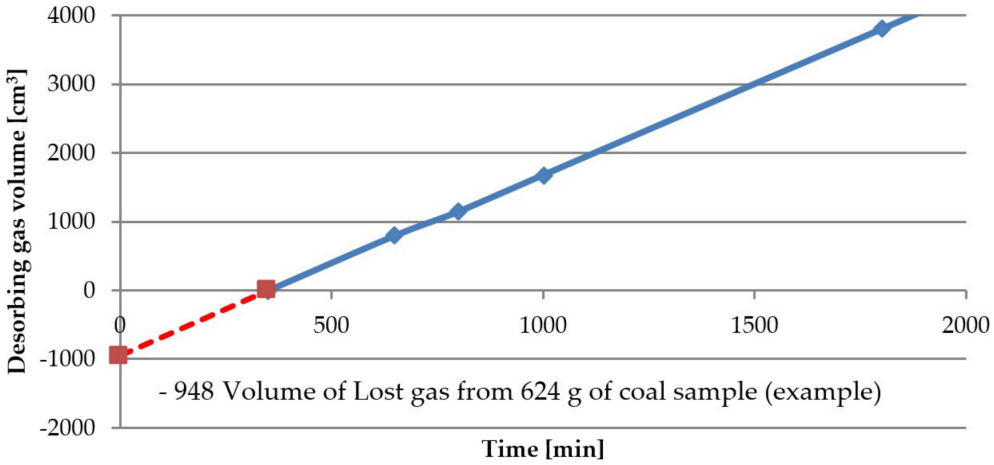

Figure 4. Lost gas volume determination in the USBM method.

Based on the obtained volumes of desorbing, residual, and lost gas and the results of chromatographic analysis taking into account the physicochemical properties, the final methane-bearing capacity value is determined. This allows the gas losses to be taken into account in a precise and characteristic manner for the prevailing conditions and properties of a given coal sample. The individual gas components and their volumes are determined with reference to a specific amount of coal sample, while the final result is always calculated into a ton of clean coal substance.

2.4. Investigation of Methane Sorption Kinetics and Isotherms

Methane sorption kinetics, sorption parameters, and methane sorption isotherms were investigated using the gravimetric method with the IGA-001 gravimetric sorption system (Figure 5). It is used to precisely analyse the magnitude of gas sorption dynamics and kinetics on porous materials.

Sorption studies were conducted using drill cuttings samples. Representative samples of coal were crushed and sieved to a fraction of 0.30–0.43 mm. The samples prepared in this way were used for sorption tests, which were carried out under stable and continuously controlled temperature conditions of 298 K. The sample mass used for sorption testing was approximately 150 mg.

Figure 5. IGA-001 gravimetric sorption system used to investigate methane sorption kinetics and methane sorption isotherms.

The sorption kinetics were analysed at a methane saturation pressure of 0.1 MPa. Sorption parameters, such as sorption capacity, effective diffusion coefficient, and half sorption time, were determined. Sorption capacity is a measure of the ability to sorb vapours and gases, is determined at sorption equilibrium, and determines the amount of gas sorbed per unit mass of the sample at a given pressure and temperature. The parameter characterizing the course of sorption kinetics (its dynamics) is the effective diffusion coefficient. Coal with a higher D_e value, assuming the same grain size of the ground coal mass, will release the same amount of gas in a shorter time. A high value of the effective diffusion coefficient should be a signal warning of a peculiar coal structure, most often resulting from proximity to geological disturbances [50,51]. The half sorption time represents the time at which the amount of gas sorbed is half the amount of total sample saturation. The above parameters are determined at the sorption equilibrium level, under the pressure of 0.1 MPa. The effective diffusion coefficient is determined based on a unipore sorption/diffusion model, which requires some simplifications [52,53], including the treatment of coal grains as spherical. An equation to determine the above coefficient was proposed by Timofiejew [54], where the time at which the gas mass is half of the initial mass is sought:

$$D_e = \frac{0.308 \times R_o^2}{\pi^2 \times t_{1/2}} \quad (3)$$

where R_o is the substitute grain radius (cm).

Methane sorption isotherms were determined at 3 pressure points: 0.1, 0.7, and 1.5 MPa. Sorption isotherm points were determined based on automated transitions to higher pressure levels after the sorption equilibrium was reached. The study was performed based on the type I sorption isotherm, the Langmuir isotherm, commonly used to describe the coal-gas system. The Langmuir sorption isotherm equation can be written as follows [52]:

$$a(p, T) = a_m \frac{p}{p_l + p} \quad (4)$$

where a is the volume of adsorbed methane at pressure p (STP) (cm^3/g_{daf}), a_m is the maximum sorption capacity at pressure $p \rightarrow \infty$ (STP) (cm^3/g_{daf}), p_l is the Langmuir half sorption pressure (MPa), and p is the equilibrium pressure of methane (MPa).

2.5. Coal Structure Investigation Based on Sorption Analyses

Parameters characterizing their structure were determined for the tested coals. Based on carbon dioxide sorption isotherms, performed at 298 K, using the Dubinin–Radushkevich model, the surface area and volume of micropores were determined. Carbon dioxide is a gas that effectively penetrates the porous structure of hard coal. The small size of the CO_2 molecule, its double dipole structure, and its low activation energy make carbon dioxide a gas that penetrates the smallest pores of coals and is often used to define the micropore system in hard coals [55–57]. The measurements were performed on samples ground to a grain size of 0.5–0.7 mm with the volumetric method in the pressure range up to 0–0.1 MPa using an ASAP 2010 apparatus from Micromeritics (Figure 6).

Figure 6. ASAP 2010 volumetric sorption analyser.

A 2 g sample of coal, before sorption measurement, was subjected to a degassing process to clean the coal surface of adsorbed vapours and gases. The sample was placed in a helium atmosphere for 24 h before degassing. Helium atoms do not sorb, and their kinetic energy allows the removal of sorbed gases from the coal surface. The degassing was carried out under a vacuum until the pressure increase over the sample was no greater than 2×10^{-1} Pa/min. The degassing temperature was 318 K. After degassing, the sample was subjected to a proper sorption test.

Carbon dioxide sorption isotherms were measured at a temperature of 298 K, similar to the conditions in coal mines, to determine the surface area and volume of micropores according to the Dubinin-Radushkevich model.

Nitrogen sorption isotherms were measured at 77.5 K to characterize the meso- and macropores occurring in the structure of the coals. Based on the nitrogen sorption isotherms, the specific surface area was determined using the BET model, and the meso- and macropore volumes were determined using the Barrett-Joyner-Halenda model. Based on the obtained results, the porosity of the analysed coals was determined.

3. Results and Discussion

3.1. Results of the Methane-Bearing Capacity Test

As part of this paper, methane-bearing capacity tests were conducted using two direct methods: the direct drill cuttings method and the United States Bureau of Mines method. Their results are shown in Table 3 and as a bar graph (Figure 7).

Table 3. Comparison of methane-bearing capacity test results obtained using the USBM method and the direct drill cuttings method with a loss factor of 1.12 and 1.33.

Sample Number	Methane-Bearing Capacity (m^3 CH_4/t_{daf})		
	Direct Drill Cuttings Method Gas Loss Factor 1.12	Direct Drill Cuttings Method Gas Loss Factor 1.33	USBM Direct Method
P-1	7.025	8.341	8.245
P-2	2.370	2.814	2.909
P-3	6.764	8.033	8.112
P-4	3.341	3.968	3.653
P-5	2.596	3.083	2.925
P-6	2.277	2.705	3.350
P-7	3.920	4.655	4.825
P-8	3.855	4.578	4.481
P-9	3.764	4.470	4.989

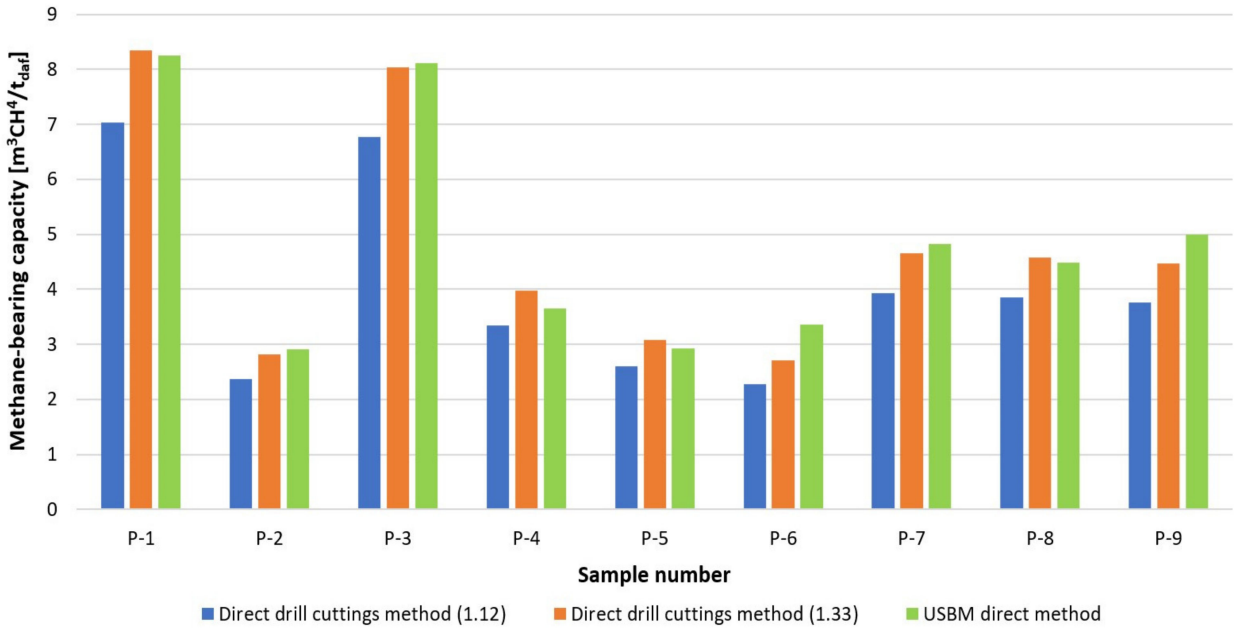

Figure 7. Graphical summary of methane-bearing capacity test results obtained using the USBM method and the direct drill cuttings method with a loss factor of 1.12 and 1.33.

The results of the methane-bearing capacity for the direct drill cuttings method are presented considering two different loss factors: 1.12 described in the Polish standard PN-G-44200:2013-10 [35] and the literature [33,34], and 1.33, which was developed, among others, within the framework of this multi-parameter analysis by the empirical method.

Based on the obtained results, it may be stated that the lowest values were found for the direct drill cuttings method with the application of the loss factor of 1.12. Their values ranged from 2.277 to 7.025 m^3 CH_4/t_{daf}. However, for the same method, using a loss factor of 1.33, the results ranged from 2.705 to 8.341 m^3 CH_4/t_{daf}. For the same coal samples, methane-bearing capacity test results using the USBM method ranged from 2.909 to 8.245 m^3 CH_4/t_{daf}. As the USBM method is more precise and accurate, it served as a reference method based on which the loss factor of 1.33 was empirically determined as the more appropriate one for compensating for gas losses at the stage of coal sampling for testing. After analysing the results, it was concluded that, with the loss factor 1.33, the results for the direct drill cuttings method are similar to those obtained by the USBM method. Similar values were found for the samples P-1, P-3, P-5, and P-8. For P-4, the methane-bearing capacity value obtained by the USBM method was 3.653 m^3 CH_4/t_{daf}, while for the direct drill cuttings method using a loss factor of 1.33 it was 3.968 m^3 CH_4/t_{daf}.

This is the only example in which the USBM result was visibly lower than that obtained by the direct drill cuttings method, but only when a loss factor of 1.33 was used. For a loss factor of 1.12, the value was higher. For the samples P-2, P-6, P-7, and P-9 the values obtained by the USBM method were visibly higher than those obtained by the direct drill cuttings method, regardless of the applied loss factor.

Accurate determination of gas losses, which is associated with proper determination of methane-bearing capacity, is of great importance in the performance of exploratory drilling and core sampling, where pulling a drill core often takes several to several dozen minutes. This is due to the necessity of pulling out individual drill rods and other technical considerations while drilling, as well as the personnel that take samples. Due to the recorded time from the start of drilling to the moment of placing the coal core in the hermetic container, it is possible to precisely determine the gas losses individually for each of the analysed coal samples in the USBM method.

3.2. Results of Methane Sorption Kinetics and Methane Sorption Isotherms

As stated in the literature [58–61], when determining the methane-bearing capacity of hard coal seams it is very important to take into account the sorption properties and the coal's ability to undergo desorption. One of the factors analysed in this paper was the effect of methane sorption kinetics on the proper determination of gas losses. Skoczylas [61] noted in his work that the kinetics of methane released from coal, in addition to the effective diffusion coefficient, which under stable thermodynamic conditions depends on the structure of the coal matrix, is also determined by the grain size used in the analysis. This means that the processes of methane release from the coal structure occur with greater dynamics as the grain class decreases. This is particularly important because, in the direct drill cuttings method, the drill cuttings are collected for testing, while in the USBM method, coal cores are collected for testing. This means that losses generated from sampling drill cuttings will be greater than from core sampling.

Table 4 presents the results of the sorption tests. The results obtained from methane sorption isotherms are summarized along with the coefficients of isotherms determined by the Langmuir model. The sorption properties concerning the analysed methane sorption kinetics are also shown along with the determined sorption capacity, effective diffusion coefficient and half sorption time. By determining the methane sorption isotherms and performing the approximation, it is possible to indirectly determine the methane-bearing capacity under saturation pressure conditions [62,63]. In the case of this analysis, no significant dependencies and no influence of the results obtained from methane sorption isotherms on gas losses were observed. Based on the analysis of methane sorption kinetics, it was possible to identify those samples for which desorption processes occurred faster, and thus the losses generated at the stage of sampling for research are higher. After analysing the obtained results of sorption capacity, it was found that this parameter does not have much influence on the proper determination of gas losses during sampling for methane-bearing capacity testing. Its greatest interpretive potential is obtained when it is juxtaposed with methane-bearing capacity. Particularly dangerous conditions in terms of gas and rock outburst hazard and methane hazard are characterized by high methane-bearing capacity with low sorption capacity. Then, conditions exist that favour the accumulation of free methane in the coal matrix [64,65]. For the analysed coal samples, the sorption capacity values ranged from 1.720 to 3.230 cm^3/g_{daf}. The highest value of 3.230 cm^3/g_{daf} was obtained for P-1, while the lowest value of 1.720 cm^3/g_{daf} was obtained for P-4.

The highest interpretative values are associated with the effective diffusion coefficient, whose value determines the rate of sorption processes in the coal-gas system. Higher values of this parameter mean higher dynamics of sorption processes, and thus also of desorption processes. Consequently, more gas is lost at the stage of coal sampling for methane analysis. The highest effective diffusion coefficient values were obtained for P-6 and P-9, which were 0.369×10^{-8} and 0.569×10^{-8} cm^2/s, respectively. A value of the effective diffusion coefficient above 0.15×10^{-8} cm^2/s indicates possible negative structural

changes in the coal or proximity to fault zones. As was observed for the mentioned samples P-6 and P-9, the methane-bearing capacity values obtained by the USBM method were visibly higher than those obtained by the direct drill cuttings method, regardless of the loss factor used. Based on the above observations, the following conclusion can be constructed. The coals with high sorption kinetics, i.e., those for which the value of the effective diffusion coefficient is high and exceeds the value of 0.15×10^{-8} cm^2/s, are characterized by high gas losses at the stage of sampling for methane-bearing capacity testing. For the analysed samples P-4 or P-5, for which lower values of the effective diffusion coefficient of 0.077×10^{-8} and 0.084×10^{-8} cm^2/s were obtained, smaller disproportions between the obtained results of methane-bearing capacity determination for the analysed methods were observed when the loss coefficient of 1.33 was applied.

Table 4. Summary of the results of methane sorption analyses: sorption isotherms and sorption kinetics.

Sample Name	Langmuir Isotherm Coefficients a(P) = (am*b*P)/(1 + b*P)		Sorption Points in Langmuir Isotherm		Sorption Kinetics		
	a_m	b	P [bar]	a [cm^3/g$_{daf}$]	a_{daf} [cm^3/g$_{daf}$]	D_e [cm^2/s]	$t_{1/2}$ [s]
P-1	20.820	0.158	0	0	3.230	0.091×10^{-8}	10,952
			1	3.23			
			7	10.82			
			15	14.71			
P-2	18.451	0.158	0	0	2.730	0.117×10^{-8}	8535
			1	2.73			
			7	9.50			
			15	13.06			
P-3	16.884	0.184	0	0	2.750	0.092×10^{-8}	10,859
			1	2.75			
			7	9.38			
			15	12.46			
P-4	15.477	0.106	0	0	1.720	0.077×10^{-8}	12,922
			1	1.72			
			7	6.45			
			15	9.57			
P-5	21.265	0.151	0	0	3.100	0.084×10^{-8}	11,797
			1	3.10			
			7	10.67			
			15	14.88			
P-6	22.636	0.135	0	0	3.090	0.369×10^{-8}	2695
			1	3.09			
			7	10.67			
			15	15.28			
P-7	16.566	0.149	0	0	2.400	0.151×10^{-8}	6610
			1	2.40			
			7	8.24			
			15	11.54			
P-8	18.962	0.159	0	0	2.840	0.097×10^{-8}	10,296
			1	2.84			
			7	9.77			
			15	13.46			
P-9	17.851	0.182	0	0	3.08	0.569×10^{-8}	1751
			1	3.08			
			7	9.68			
			15	13.23			

The values of the half sorption time $t_{1/2}$, which represents the time when the amount of gas sorbed is half the amount of total sample saturation, were also analysed. It is a parameter that, similarly to D_e, determines the rate of sorption processes, and its value is

given in seconds. For the samples P-6 and P-9 analysed above, which show high kinetics of sorption processes, the values of $t_{1/2}$ were 2695 and 1751 s, respectively. The low values of half sorption time indicate a potentially high gas loss, which is related to the rapid gas release by the coal structure and the dynamically reached sorption equilibrium state. In comparison, slower desorption is evident for P-4 and P-5, for which the determined half sorption times were 12,922 and 11,797 s, respectively.

3.3. Results of Hard Coal Structure Analysis

The studied coals are characterized by differentiated structures. The surface area values, according to the Dubinin-Radushkevich model, are in the range of 80.55–170.70 m^2/g, and the volume of micropores is 0.032–0.068 cm^3/g.

The proportion of meso- and macropores was determined from nitrogen sorption isotherms analysed at 77.5 K. At 77.5 K, nitrogen molecules enter only the meso- and macropores bypassing the micropore system due to coal shrinkage and very small kinetic energy values of nitrogen molecules [19,57,66]. The surface area values determined from the BET model range from 0.46–2.62 m^2/g, and the pore volume according to the BJH method ranges from 0.00057–0.00299 cm^3/g. A summary of the coal structure investigation is presented in form of Table 5.

Table 5. Summary of the results of coal structure investigation.

Sample Name	Surface Area D-R [m^2/g]	Micropore Volume D-R [cm^3/g]	Average Pore Radius DA [nm]	Surface Area BET [m^2/g]	Mezo and Macropore Volume BJH [cm^3/g]	Porosity [%]
P-1	126.51	0.051	0.887	0.66	0.00060	3.66
P-2	95.19	0.038	0.895	0.46	0.00057	2.07
P-3	105.21	0.042	0.953	0.99	0.00140	2.71
P-4	80.55	0.032	1.058	0.78	0.00092	1.91
P-5	170.70	0.068	0.874	2.62	0.00202	4.71
P-6	162.96	0.065	0.876	2.08	0.00299	5.08
P-7	97.81	0.039	0.973	0.76	0.00088	2.18
P-8	119.14	0.048	0.843	0.78	0.00081	2.80
P-9	127.71	0.051	0.878	1.21	0.00192	2.65

Porosity was also determined for the tested coals as the ratio of the volume of pores determined from carbon dioxide sorption to the volume of the tested sample during the measurement conditions, i.e., at the pressure of 0.1 MPa. The obtained porosities are in the range 1.91–5.08%.

P-4, for which the result of the USBM methane-bearing capacity determination was exceptionally lower than the results obtained by the direct drill cuttings method, is the coal with the lowest values of surface area and volume of micropores determined according to the D-R model. Meanwhile, the values of the surface area estimated by the BET model and pore volume by the BJH model are low. This coal has a poorly developed and inaccessible structure and, consequently, its sorption capacity is low for both carbon dioxide and nitrogen. Pore constrictions which effectively inhibit the free flow of gas within the pore structure are probably present. The low accessibility of the P-4 carbon structure to gas translates into overall desorption difficulty, as evidenced by the largest half-time (12,922 s) and the lowest value of effective diffusion coefficient (0.077×10^{-8} cm^2/s) among the studied coals.

In the case of P-6 and P-9, the differences in the determination of methane-bearing capacity by the borehole method at both loss compensation factors and USBM are the largest among the coals studied. The differences in the results reach up to 30%. The effective diffusion coefficients of these coals are the highest, which is related to rapid desorption and significant gas losses. Both of these coals are characterized by a well-developed transport pore system (meso- and macropores) in addition to large micropore volumes. This is

evidenced by large surface area values according to the BET model and larger pore volumes than the other coals according to the BJH method. The extensive transport pore system facilitates gas desorption from the coal structure. It is worth mentioning that P-6 has the highest porosity and gas loss is the highest in its case.

Significant differences in the determination of methane-bearing capacity between the methods described were also observed for P-2 and P-7. The desorption process for these coals occurs fairly quickly. The values of effective diffusion coefficients are higher than for the other coals but lower than for P-6 and P-9. It was observed that these coals are already characterized by a significantly smaller microporous volume than the P-6 and P-9 samples. The meso- and macropore volumes are also smaller and the structure of the coals is more compact.

Therefore, it can be assumed that the volume of micropores is not a determining factor in influencing the amount of gas loss. P-2 and P-7 with small surface area values according to the D-R model have higher gas losses than coals with much larger surface area values, or micropore volumes, such as P-1 or P-5.

Additionally, noteworthy is the P-5 coal with the highest values of microporosity volume and surface area and a very well-developed system of meso- and macropores (the highest surface area according to BET). Despite the greatly expanded pore system and large transport pore volumes, methane desorption occurs slowly. The value of the effective diffusion coefficient of this carbon is low, it has a long half time of sorption and less gas loss. The determined sorption capacity for this coal sample is also high, confirming its extended structure. Methane-bearing capacity is determined in the inverse of the sorption-desorption process, and in addition to the specific surface area of coals, there are many other factors that determine its value (including sorption kinetics, pressure difference, coal bed pressure, etc.). Not always coals with a well-accessible structure for the sorbed gas, and such a value was determined by the surface area and pore volume, show a high value of methane-bearing capacity. An example of such coal is P-5 coal, for which despite the developed structure (measured by the availability of coal structure for the sorbed gas in the conducted measurement conditions) the process of methane desorption occurs relatively slowly.

Analysing the results of the study, no clear correlation can be observed between the parameters characterizing the structure of coals and the gas losses occurring during sampling. The most important aspect in the evaluation of gas losses appears to be the sorption kinetics as expressed by the effective desorption coefficient, or half sorption time.

No clear relation between the amount of desorbed gases and the structure of coals or their properties was confirmed in Dudzińska's work [67]. The authors of this work found that coals with a lower degree of metamorphism, a more extensive pore system, including transport pores, and a loose structure do not always show a greater propensity to desorb gases from coals.

3.4. Final Discussion

It was found that the methane-bearing capacity determined by the USBM method is higher than that obtained by the direct drill cuttings method. In addition to the result of the methane-bearing capacity test, which precisely takes into account the gas losses, the USBM tests provide information on the volume of the constituent gases, i.e., desorbed, residual, and lost gas, as well as on the composition of these gases obtained by chromatographic analysis. The USBM method was found to be the most precise method to take into account individual gas losses for each analysed sample. The most similar values are obtained for the direct drill cuttings method using a loss compensation factor of 1.33. It was found that methane sorption kinetics has a very important influence on the proper determination of methane-bearing capacity, which was also reported in the literature [2,68,69]. Samples for the USBM method are taken in the form of a core, which to some extent reduces the losses that are generated when taking drill cuttings samples for the direct drill cuttings method. The USBM method, even though it seems to be the most precise and accurate, also has a disadvantage, which is the analysis time. With the direct drill cuttings method,

test results can be obtained up to 24 h, while with the USBM method, free core desorption takes from 2 weeks up to 2 months. The proposal to use a new coefficient for gas loss resulted from uncertainty about the coefficient currently used in the Polish standard for the direct drill cuttings method. It often does not correspond to the actual amount of gas lost during sampling for testing. The currently used coefficient is 1.12, while a new coefficient of 1.33 has been proposed, which was taken from the empirical analysis and observation of the results obtained by the USBM method, in which gas losses are precisely determined. Observing the results obtained for the USBM method, it was determined that the most similar values for the direct drill cuttings method give results that are increased by a factor of 1.33. In the USBM method, no loss factor is used, due to the fact that the losses in this method are determined individually for each of the analysed samples.

Given the above, the direct drill cuttings method, otherwise known as the single-phase vacuum degassing method, seems to be appropriate for routine control of the methane hazard state in hard coal mines. The USBM method is appropriate for the assessment of the amount of methane resources in hard coal seams, the possibility of its extraction, and for modelling the methane deposits or carrying out verification of methane-bearing capacity determination for longwalls.

4. Conclusions

This paper presents the results of conducted research on gas losses that are generated at the stage of coal sampling for methane-bearing capacity testing. A multi-parameter analysis was conducted in which methane-bearing capacity tests were performed using two methods, the United States Bureau of Mines method and the direct drill cuttings method. Sorption studies were also conducted to determine methane sorption isotherms and isotherm coefficients in the Langmuir model, methane sorption kinetics studies, and pore structure studies. Based on the conducted multi-parameter analysis, the following conclusions were constructed:

- For the coal samples analysed, the methane-bearing capacity results obtained by the United States Bureau of Mines method showed higher values than those obtained by the direct drill cuttings method, which used a loss factor of 1.12.
- The United States Bureau of Mines method was used as a reference method in which gas losses are determined accurately and individually for each coal sample analysed.
- A very important aspect to consider when determining gas losses at the coal sampling stage for methane-bearing capacity testing is its sorption kinetics. The parameters that best describe the kinetics of sorption processes are the effective diffusion coefficient and the half sorption time.
- The structural parameters associated with the hard coal pore system do not significantly affect the rate of gas desorption. Therefore, they do not affect the correct determination of gas losses during methane-bearing capacity tests.
- Based on the multi-parameter analysis performed, a gas loss compensation factor of 1.33 was determined, which is recommended for use when determining methane-bearing capacity using the direct drill cuttings method.
- The direct drill cuttings method, otherwise known as single-phase vacuum degassing, can be applied for routine control of the methane hazard in hard coal mines. The USBM method seems to be more appropriate for the estimation of methane resources in hard coal seams, possibilities of its exploitation, and for modelling the deposit or carrying out verification of methane-bearing capacity determination for longwalls.

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