

Article

The Repeatability of Sorption Processes Occurring in the Coal-Methane System during Multiple Measurement Series

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Abstract: The aim of this paper was to investigate the repeatability of sorption processes occurring in the coal-methane system during multiple measurement series. For research purposes, three granular samples of coal sorbent were used. The samples were subjected to a series of three measurements, each time performed under the same conditions. During each series of measurements, the following stages took place: outgassing the sample in a vacuum, and then saturating it with methane under the pressure of 1, 3, and 10 bar. Sorption capacities and the values of effective diffusion coefficients were compared. The studies into the repeatability of measurements of sorption capacities, conducted by means of the IGA-001 (Intelligent Gravimetric Analyzer) gravimetric instrument for three measurement cycles, showed that the obtained measurement discrepancies in relation to the mean value did not exceed 1.23%. The discrepancies in question approximated the measurement uncertainty of the IGA-001 device. The evaluation of the recurrence of determining the values of effective diffusion coefficients showed that the obtained discrepancies were no larger than 10%, which might have resulted from problems with fulfilling most of the assumptions of the applied unipore diffusion model. The authors did not observe any changes of the sorption parameters of hard coal during consecutive cycles of methane saturation.

Keywords: repeatability of sorption processes; sorption equilibrium; sorption capacity; coal-methane system; diffusion coefficient

1. Introduction

The sorption capacities of porous media are of vital importance for numerous aspects of both scientific and engineering-related research. One sorbent-sorbate system frequently occurring in nature is the hard coal-methane system. Studies into this system focus on the safety of coal exploitation under the conditions of methane hazards, obtaining methane from coal seams, locating carbon dioxide in coal seams and underground gasification [1–7]. In a laboratory, a coal sample is often subjected to cyclical processes of sorption/desorption. Many researchers signalled that systematic saturation of coal with methane and outgassing it to a vacuum lead to changes in the basic sorption parameters [8,9]. According to the suggestions of the authors, these changes are caused by the effect of the sorption-induced swelling of coal, which results in some structural changes in the coal substance, leading to the enlargement of the sorption area. Such a phenomenon may be easily interpreted as a systematic increase in the availability of consecutive pores within the complex coal structure for penetration with gas molecules. This would also result in changes to the parameters describing the kinetics of the methane sorption in coal.

The comparison of high pressure (up to 7 MPa and 15 MPa) sorption measurements of the coal-carbon dioxide system, performed using gravimetric and volumetric methods by six independent laboratories, was discussed in the works [10,11]. The differences of the results of the sorption capacities obtained by the laboratories amounted to 100%. Such large discrepancies in the results were accounted for by the differences of the measurement procedures of particular research methods. More comparative CO₂ sorption studies on hard coal, using the manometric and the gravimetric method, were conducted by three European laboratories [12]. At a pressure of up to 3 MPa, the differences in the readings among the laboratories did not exceed 2%. At the pressure of 3–6 MPa, the differences of sorption capacities were up to 5%, at pressures of 6–16 MPa, the differences in the results amounted to 25%.

Sorption-related analysis of the solid-gas system poses a considerable metrological problem. The complexity of the processes of gas accumulation/emission within the porous structure of a solid is immense. The process of gas accumulation/emission, analyzed in relation to a porous solid and often called sorption/desorption, is, in fact, a compilation of processes of transportation and sorption proper, understood as reducing the number of degrees of gas molecule freedom due to surface interactions [13]. The mechanisms of gas transportation occurring within the porous structure of the sorbent can be viewed as:

- filtration—driven by the pressure gradient (macropores and fissures),
- diffusion—driven by the concentration gradient (micropores).

Transportation occurring inside singular, small sorbent grains can be viewed as diffusion. The basic physical relation describing the diffusion process quantitatively is Fick's second law [14]:

$$\frac{\partial \phi}{\partial t} = D \cdot \nabla^2 \phi, \quad (1)$$

where: $\phi \left[\frac{\text{mol}}{\text{m}^3} \right]$ —is the substance concentration, t [s]—is time, $D \left[\frac{\text{m}^2}{\text{s}} \right]$ —is the diffusion coefficient.

The physical model most frequently used in determining the effective diffusion coefficient is the unipore model [15]:

$$\frac{\partial \phi(r, t)}{\partial t} = \frac{D}{1+H} \cdot \nabla^2 \phi(r, t) = D_e \cdot \nabla^2 \phi(r, t), \quad (2)$$

where: $D_e \left[\frac{\text{m}^2}{\text{s}} \right]$ —is the effective diffusion coefficient $D_e = \frac{D}{1+H}$, $H[-]$ —is the slope coefficient in Henry's sorption isotherm, r [m]—is the distance from the centre of the grain.

An analytical solution to Equation (2), fulfilling a substantial number of the assumptions of the unipore model, can be found, among others, in works by [15,16]:

$$\frac{a(t)}{a_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \cdot D_e \cdot \pi^2 \cdot t}{R_0^2}\right), \quad (3)$$

where: a_∞ [mol]—is the total amount of gas sorbed in grains, $a(t)$ [mol]—is the amount of gas sorbed in the moment t , R_0 [m]—is the substitute grain radius determined on the basis of the following relation: $R_0 = \frac{1}{2} \sqrt[3]{\frac{2 \cdot d_1^2 \cdot d_2^2}{d_1 + d_2}}$, where: d_1 and d_2 are the limits regarding the size of grains from the analyzed grain fraction. After solving Equation (3) for the time in which the amount of the sorbed gas constitutes half the final amount:

$$\frac{6}{\pi^2} \left(\exp\left(-\frac{D_e \cdot \pi^2 \cdot t}{R_0^2}\right) + \frac{1}{2^2} \exp\left(-\frac{2^2 \cdot D_e \cdot \pi^2 \cdot t}{R_0^2}\right) + \frac{1}{3^2} \exp\left(-\frac{3^2 \cdot D_e \cdot \pi^2 \cdot t}{R_0^2}\right) + \dots \right) = \frac{1}{2},$$

one can obtain Timofeev's Formula [16]:

$$D_e = \frac{0.308 \cdot R_0^2}{\pi^2 \cdot t_{1/2}}, \quad (4)$$

where: $t_{1/2}$ [s]—is the half-time of the process.

From Formula (4), one can determine the effective diffusion coefficient of the analyzed sorbent, on the basis of the registered kinetics of the sorption process. The parameters a_∞ and D_e from the Formula (3), for the coal-methane system, are extremely important when it comes to evaluating gas hazards and outburst hazards in hard coal mines [17]. Also, they constitute a basis for model analyses and laboratory research regarding carbon dioxide sequestration and the process of obtaining methane from coal seams [18–20].

Laboratory research into hard coal very often involves subjecting a sample to repeated gas sorption/desorption processes. Such research includes:

- determining sorption isotherms in various temperatures [21,22],
- experiments on exchange sorption of CO₂/CH₄ [19,23,24],
- analysing the kinetic properties of accumulation and emission of coal sorbate [25,26],
- sorption tests on samples under mechanical stress, taking into account swelling and shrinking of coal [27,28],
- tests determining the influence of moisture content in coal on sorption [29,30].

If a single cycle of the example sorption tests resulted in permanent changes in the sorbent, it would be necessary to supply “fresh” coal material every single time.

The authors set out to check if hard coal would change its sorption properties—represented by the sorption capacity under different pressure values and by the effective diffusion coefficient—when the processes of sorption/desorption are repeated numerous times. In order to ensure clarity of results, a measurement procedure was developed, comprising of a series of three repetitions consisting of outgassing the sample to a vacuum and, subsequently, saturating it with methane until the moment when the sorption equilibrium is reached. Four high-volatile hard coal samples were used.

As the physics of the phenomena of methane sorption and transportation in coal is complex, and since registering these phenomena can be burdened with metrological problems, it is extremely important to determine if numerous cycles of sorption/desorption are accompanied by repeatable and oriented changes in the sorption capacity and an effective diffusion coefficient. This paper tries to answer the question about the value of analyzing the phenomenon of sorbent regenerative abilities in the case of research into the coal-methane system.

2. The Measuring Equipment

The research into the repeatability of sorption processes occurring in the solid-gas system, for numerous measurement cycles, was conducted by means of the gravimetric method [31]. The IGA-001 instrument (by Hiden Isochema, Warrington, UK, year of production: 2010) makes it possible to conduct sorption analyses under both isobaric and isothermal conditions. The measurement performed with the IGA-001 instrument involves observing changes of the sample mass, caused by gas sorption processes occurring within the sample. The instrument makes it possible to determine the sorption isotherms of vapors and gas for any sorbent, as well as to analyze the kinetics of sorption processes. Moreover, the IGA-001 device allows us to determine the specific surface area of the sorbent, its porosity and pore size distribution, as well as to conduct absorption analyses. In the research described here, the instrument was used to determine sorption capacities and to analyze the kinetics of methane sorption in hard coal samples. The schematic representation of the structure of IGA-001 is presented in Figure 1, and a photograph of the instrument is presented in Figure 2.

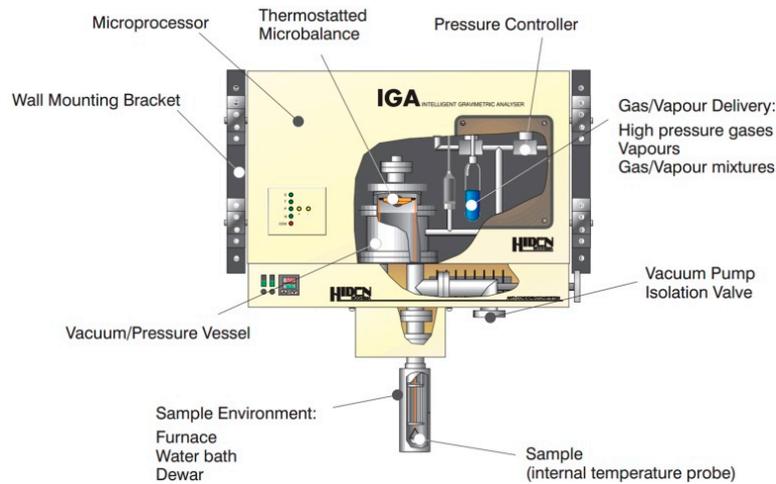


Figure 1. The structure of the IGA-001 instrument—a schematic representation.



Figure 2. The IGA-001 gravimetric instrument—a photograph.

The measurement procedure carried out with the IGA-001 device is based on registering changes in the sorbent mass, under constant temperature and gas pressure. This is a gravimetric method which requires compensating the buoyant force. The amount of the sorptively bonded gas can be determined from the formula referring to the equation of state for a real gas:

$$\begin{aligned}
 n &= \frac{p \cdot V_g}{z \cdot R \cdot T}, \\
 n &= \frac{p}{z \cdot R \cdot T} \cdot \left(\frac{m(t) - m_0 + m_b}{\rho_g} \right), \\
 a &= \frac{p}{z \cdot R \cdot T} \cdot \left(\frac{m(t) - m_0 + m_b}{\rho_g \cdot m_0} \right) \cdot V_m.
 \end{aligned} \tag{5}$$

where: n [mol], a $\left[\frac{\text{m}^3}{\text{g}} \right]$ —is the sorption determined with the IGA-001 instrument, p [Pa] is the gas pressure, V_g $[\text{m}^3]$ —the amount of gas sorptively bonded in a sample, $m(t)$ [g], m_0 [g]—is the instantaneous and the original mass of the sample, m_b [g]—is the correction compensating the buoyant

force, $V_m \left[\frac{\text{m}^3}{\text{mol}} \right]$ is the molar volume of gas (under normal conditions), $R \left[\frac{\text{J}}{\text{mol}\cdot\text{K}} \right]$ —is the universal gas constant, $T [\text{K}]$ —is the temperature, $z [-]$ —is the gas compressibility coefficient.

The measurement uncertainty of the IGA-001 is not specified by the manufacturer. The measurement uncertainty is related to the accuracy of the microscales measuring the sample mass m and the uncertainty of the correction compensating the buoyant force m_b . The resolution of the microscales in the IGA-001 instrument is 0.2 μg , which—in the measuring range of 0–100 mg—makes it possible to neglect the uncertainties of the sample mass measurement in relation to the uncertainties of the other parameters of Equation (5). The gravimetric measurements call for considering the buoyant force m_b exerted by gas on the analyzed sorbent sample. The correction compensating the buoyant force m_b added to the readings of the microscales can be expressed with the following formula:

$$m_b = \frac{m(t) \cdot p \cdot M}{\rho_s \cdot z \cdot R \cdot T}, \quad (6)$$

where: $M \left[\frac{\text{g}}{\text{mol}} \right]$ —is the molar mass of gas, $\rho_s \left[\frac{\text{g}}{\text{m}^3} \right]$ —is the sample density.

The uncertainty of determining the m_b correction is equal to the relative deviations of the parameters in Formula (6), and can be calculated as an exact differential:

$$u(m_b) = m_b \cdot \sqrt{\left(\frac{u(m)}{m}\right)^2 + \left(\frac{u(p)}{p}\right)^2 + \left(\frac{u(\rho_s)}{\rho_s}\right)^2 + \left(\frac{u(T)}{T}\right)^2}. \quad (7)$$

In Formula (7), determining the uncertainty compensating the buoyant force, the following uncertainty constituents can be neglected:

- the sample mass $u(m) \approx 0$ —due to the high accuracy of the microscales in the IGA-001 instrument,
- the gas pressure $u(p) = 0.008$ bar (ca. 0.04%)—due to the accuracy of the applied precise pressure transducer and the high precision of the process of pressure stabilization during the measurement (± 0.002 bar),
- temperature $u(T) \leq 0.03$ K (ca. 0.01%)—due to the precision of the process of temperature stabilization by means of the thermostat built in the IGA-001 device.

Therefore, the measurement uncertainty of the IGA-001 instrument, corresponding to the uncertainty of the process of determining the correction compensating the buoyant force, is mainly the result of the uncertainty of determining the sample density. Thus, the uncertainty of the process of determining sorption by means of the IGA-001 instrument can be expressed by the following formula:

$$u(a) = u(m_b) = F_B \cdot \sqrt{\left(\frac{u(\rho_s)}{\rho_s}\right)^2} = \frac{m(t) \cdot p \cdot M}{\rho_s \cdot R \cdot T} \cdot \sqrt{\left(\frac{u(\rho_s)}{\rho_s}\right)^2}. \quad (8)$$

3. The Research Material

For the sake of the comparative sorption studies, the authors chose four granular high-volatile hard coal samples from the “Pniówek” and “Budryk” hard coal mines located in the Upper Silesian Coal Basin in Poland. The basic parameters of the samples are shown in Table 1.

Table 1. The parameters of the samples used in sorption analyses.

Sample No.	Sample Origin—Hard Coal Mine	Grain Fraction [mm]	Sample Mass [g]	Ash Content [%]	Humidity Content [%]	Volatile Parts Content [%]
198	“Pniówek”	0.20–0.25	0.481	10.14	1.22	23.52
202	“Budryk”	0.20–0.25	0.442	3.38	1.27	30.78
205	“Budryk”	0.20–0.25	0.443	2.64	1.17	29.12
221	“Budryk”	0.20–0.25	0.474	1.90	1.24	30.75

Since the density of the coal samples used in sorption analyses was not measured, the mean density for all the analyzed samples $\rho_s = 1.34 \text{ g/cm}^3$ was adopted. The mean density was burdened by the uncertainty $u(\rho_s) = 0.027 \text{ g/cm}^3$. Thus, using Formula (8), the measurement uncertainty of the conducted sorption analyses was determined from the formula:

$$u(a) = \frac{m(t) \cdot p \cdot M}{\rho_s \cdot R \cdot T} \cdot \sqrt{\left(\frac{0.027}{1.34}\right)^2} = \frac{m(t) \cdot p \cdot M}{\rho_s \cdot R \cdot T} \cdot 0.02. \quad (9)$$

4. The Measurement Procedure

The condition necessary for conducting comparative studies is ensuring repeatability during the process of sample preparation and during research itself. To this end, a measurement procedure was developed. For each sample subjected to measurements, the procedure was repeated three times. Before each measurement series for every analyzed sample was initiated, the sample had to be properly prepared. This entailed sieving the right grain fraction and the right mass of the analyzed material. Then, the object of the analysis was placed in the IGA-001 instrument. Subsequently, the measurement procedure was initiated. This comprised of the following stages:

1. Outgassing the coal sample to the vacuum of ca. 10^{-6} mbar, for 24 h at a temperature of 353 K;
2. Saturating the sample with methane under the pressure of 1 bar, for 24 h;
3. Saturating the sample with methane under the pressure of 3 bar, for 24 h (in the case of sample no. 198, this stage was neglected);
4. Saturating the sample with methane under the pressure of 10 bar, for 24 h.

Outgassing the sample using of a turbomolecular pump for 24 h at a temperature of 353 K ensured removal of moisture from the coal before the proper tests. Thus, the impact of the moisture content on the results could be excluded. Since the sorption capacity depends on temperature [22,32], all the measurements were conducted under both isothermal and isobaric conditions (Table 2). The sorbing gas was methane.

Table 2. Measurement conditions for a singular measurement series.

Sample No.	Saturation Pressure [bar]	Temperature [K]
198	1 → 10	298
202	1 → 3 → 10	313
205	1 → 3 → 10	313
221	1 → 3 → 10	313

The main purpose of the conducted measurements was to analyze the repeatability of sorption measurements. Each sample destined for analysis was subjected to a series of three measurements, performed under identical conditions. The compared entities were sorption capacities and the values of the effective diffusion coefficients determined from Formula (4).

Before saturation and after saturating the samples with methane three times, each sample was subjected to the process of low pressure gas adsorption using the ASAP 2020 volumetric analyzer (Micromeritics Instrument Corp, Norcross, GA, USA). Before the measurement, the samples were outgassed under conditions close to vacuum (10 μmHg). The temperature was 313 K and the outgassing process lasted two hours. The temperature of the measurement was 77 K and the pressure range was 0–1 bar ($0 \leq p/p_0 \leq 1$). The adsorbate was nitrogen (N_2). The surface area (Langmuir, BET, BJH ads/des) of the coal samples was determined, as well as the total volume, average size and distribution of the pores in these samples. By means of the low-pressure gas adsorption method, basic structural parameters of the coals were established. Additionally, changes of these parameters occurred as a result of multiple saturation of the coals with methane.

5. Results

5.1. The Repeatability of Determining Sorption Capacities

According to the determined measurement procedure, each measurement—under specific pressure conditions—lasted 24 h. For the grain fraction of the analyzed samples (0.20–0.25 mm) and the values of the effective diffusion coefficients within the range of $D_e = 10^{-10} - 10^{-8} \frac{\text{cm}^2}{\text{s}}$, typical of the coals from the Upper Silesian Coal Basin, the 24-h period was considered long enough to reach the state approximating the conditions of the sorption equilibrium. In the final stage of the sorption process, the deviation from the state of the sorption equilibrium diminishes according to the formula resulting from (3):

$$\frac{a_\infty - a(t)}{a_\infty} \approx \frac{6}{\pi^2} \cdot \exp(-W \cdot t), \quad (10)$$

where: $W \left[\frac{1}{\text{s}} \right] = \frac{D_e \cdot \pi^2}{R_0^2}$.

The lower the value of the diffusion coefficient, the slower the sorption process. For hard coal with the diffusion coefficient of $D_e = 10^{-9} \frac{\text{cm}^2}{\text{s}}$, the value of the exponent from Formula (10) is ca. $W \approx 0.3 \left[\frac{1}{\text{h}} \right]$. In such a case, it can be expected that the deviation from the sorption equilibrium after 24 h shall not exceed 1%. In the case of higher diffusion coefficients, the deviation shall be even smaller. Thus, it can be concluded that after 24 h of saturation, the reached state is close to the conditions of the sorption equilibrium.

The analyses of the repeatability of determining sorption capacities involved repeating the same measurement procedure three times, using the same coal material of the analyzed sample. The repeatability was performed with the IGA-001 gravimetric device. Table 3 presents the results of the repeatability of determining sorption capacities, together with the statistical analysis and measurement uncertainties. In the consecutive columns of Table 3, one can find:

1. Sample no.,
2. p [bar]—the measurement pressure,
- 3–5. $a_1, a_2, a_3 \left[\frac{\text{cm}^3}{\text{g}} \right]$ —sorption capacities determined in the 1st, 2nd, and 3rd measurement series,
6. $\bar{a} \left[\frac{\text{cm}^3}{\text{g}} \right]$ —the mean sorption capacity from the series 1, 2, and 3, determined from the following formula:

$$\bar{a} = \frac{a_1 + a_2 + a_3}{3},$$

7. $x_a \left[\frac{\text{cm}^3}{\text{g}} \right]$ —the mean uncertainty determined from the following Formula [33]:

$$x_a = \frac{|a_1 - \bar{a}| + |a_2 - \bar{a}| + |a_3 - \bar{a}|}{3}, \quad (11)$$

8. $\frac{x_a}{\bar{a}} \cdot 100\%$ [%]—the relative mean uncertainty of the repeatability of the sorption measurement,
9. $u(a)$ —the uncertainty of determining sorption capacity with the IGA-001 instrument, calculated from Formula (9). The uncertainty in question was established for the 1st series, but for the 2nd and 3rd cycle its value was similar; thus, the measurement uncertainty for the 1st series was regarded as representative,
10. $\frac{u(a)}{a_1} \cdot 100\%$ [%]—the relative mean uncertainty of determining sorption capacity with the IGA-001 instrument.

The discrepancies in determining sorption capacities with the IGA-001 instrument, for the measurement series that was repeated three times, did not exceed 1.23% in relation to the mean value. As can be seen in Table 3, during the conducted research, the authors did not observe any considerable changes in sorption capacities resulting from the threefold repetition of the cycle of

outgassing the sample in the vacuum and saturating it with methane. What is more, the discrepancies in the results of sorption capacities, obtained in the three-measurement series, were close to the uncertainty of the sorption measurement performed with the IGA-001 instrument: ($x_a \approx u(a)$).

The courses of the threefold saturation of all coal samples with methane are presented in Figure 3.

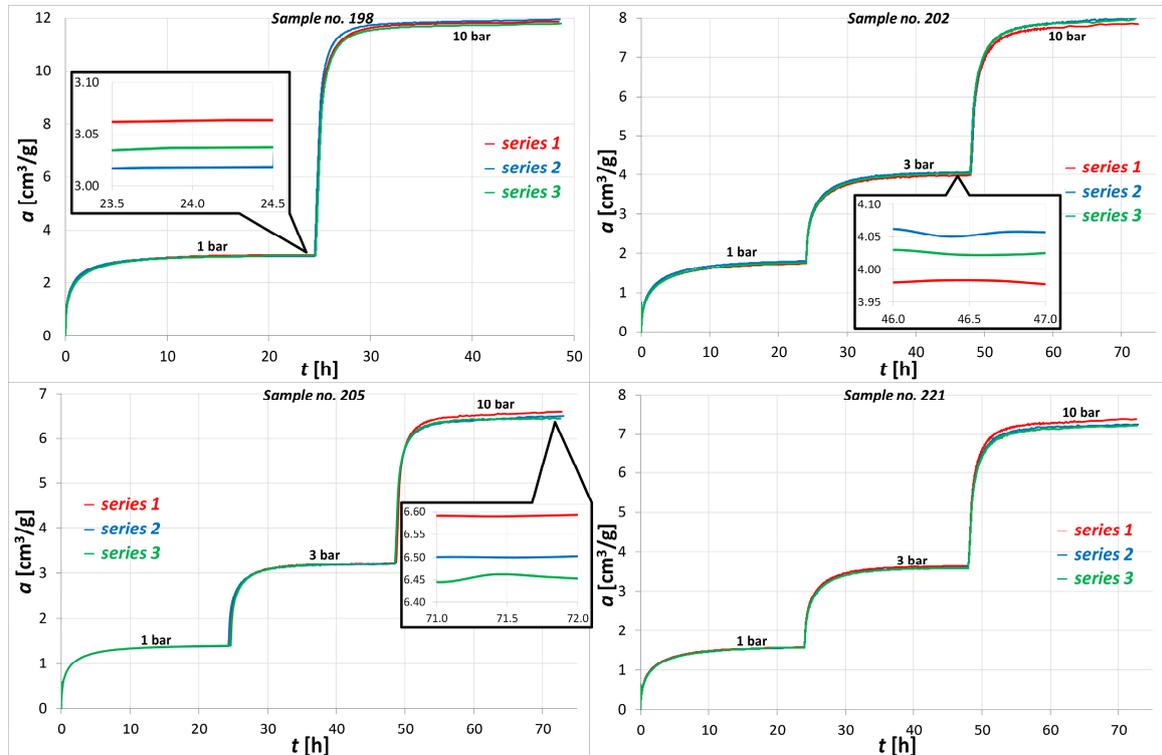


Figure 3. The compilation of the courses of threefold saturation of coal samples with methane.

As can be seen in Figure 3, no tendency regarding possible changes of sorption capacities in consecutive saturation series was observed. For the sake of clarity, the range of measurement uncertainties was not depicted in the graphs.

In order to observe changes in the pore structure of the coal material before and after saturating the samples with methane during a triple repetition cycle, nitrogen adsorption (N_2 , 77 K) measurements were carried out. The adsorption equilibrium points for particular samples before and after saturating them with CH_4 during a triple repetition cycle had similar values. All the obtained isotherms represented type IV, which indicates the mesopore character of the available pores. In samples 198 (“before” and “after”), hysteresis loops were observed, whose shape testified to the occurrence of capillary condensation between pore walls, as well as to their slotted character. In the remaining samples (202, 205, 221), no hysteresis loops were observed. This could be due to the fact that sample 198 was of different origin. Figure 4 shows the distribution of pores in all samples. In particular samples, distribution of the size of pores before and after saturating them with CH_4 is very similar, which proves that the process of saturation has no impact on the pore structure of the samples.

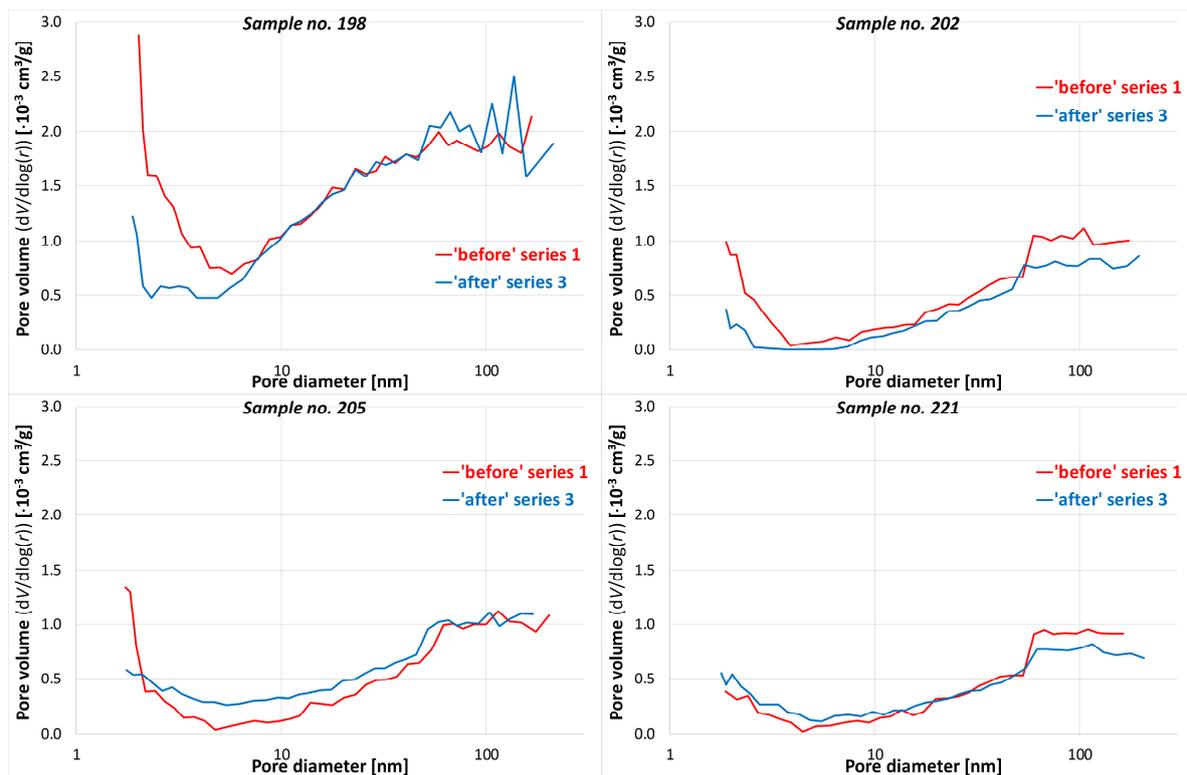


Figure 4. The pore size distribution of the samples before and after saturating them with CH_4 during a triple repetition cycle.

On the basis of the equilibrium points, structural parameters were determined, which were presented in Table 4. The values obtained for the available surface area—a feature of the micropore structure of the sample (the Langmuir model)—were $0.43\text{--}2.38\text{ m}^2/\text{g}$. The parameter of the multilayer surface area, determined according to the BET model, had a value of $0.28\text{--}1.14\text{ m}^2/\text{g}$, and the same parameter was determined according to the BJH model—describing the mesopores in the samples—had a value of $0.13\text{--}1.14\text{ m}^2/\text{g}$. The correlation index in the Langmuir and BET models was in the range of $0.991\text{--}0.999$. The values of the parameters of the surface area for samples 198 and 202 increased slightly after the process of saturating the coal material with CH_4 , and decreased in the case of samples 205 and 221. The total volume of the pores in the coal samples before saturating them with CH_4 fell in the range of $(0.84\text{--}2.86)\cdot 10^{-3}\text{ cm}^3/\text{g}$, and after the saturation process it was in the range of $(0.76\text{--}3.59)\cdot 10^{-3}\text{ cm}^3/\text{g}$. The average diameter of the pores in all the samples was $4.7\text{--}6.2\text{ nm}$, with the assumption that the samples have a slotted shape.

Table 3. The results of the repeatability of determining sorption capacities, obtained with the IGA-001 instrument, for the measurement series repeated three times.

1	2	3	4	5	6	7	8	9	10
Sample no.	Pressure	Series 1	Series 2	Series 3	Mean	Mean uncertainty of measurement repeatability, determined from Formula (11)	Relative uncertainty of measurement repeatability	Uncertainty of determining sorption capacity with the IGA-001 instrument, calculated from the Formula (9)	Relative mean uncertainty of determining sorption capacity with the IGA-001 instrument
	p [bar]	a_1 [$\frac{\text{cm}^3}{\text{g}}$]	a_2 [$\frac{\text{cm}^3}{\text{g}}$]	a_3 [$\frac{\text{cm}^3}{\text{g}}$]	\bar{a} [$\frac{\text{cm}^3}{\text{g}}$]	x_a [$\frac{\text{cm}^3}{\text{g}}$]	$\frac{x_a}{\bar{a}} \cdot 100\%$ [%]	$u(a)$ [$\frac{\text{cm}^3}{\text{g}}$]	$\frac{u(a)}{a_1} \cdot 100\%$ [%]
198	1	3.06	3.02	3.04	3.04	0.016	0.52	0.013	0.42
	10	11.86	11.94	11.79	11.86	0.054	0.46	0.128	1.08
202	1	1.76	1.82	1.78	1.79	0.022	1.23	0.011	0.62
	3	3.99	4.08	4.04	4.04	0.029	0.72	0.033	0.82
	10	7.91	8.04	7.99	7.98	0.046	0.58	0.108	1.37
205	1	1.39	1.39	1.39	1.39	0.003	0.22	0.011	0.80
	3	3.23	3.20	3.22	3.22	0.010	0.31	0.033	1.04
	10	6.60	6.51	6.45	6.52	0.051	0.78	0.111	1.69
221	1	1.59	1.59	1.58	1.59	0.002	0.13	0.012	0.73
	3	3.63	3.60	3.58	3.60	0.019	0.53	0.035	0.95
	10	7.41	7.25	7.21	7.29	0.078	1.07	0.115	1.56

Table 4. Structural properties of the samples from the N₂ gas adsorption (77 K).

Properties	Unit	198		202		205		221	
		"Before"	"After"	"Before"	"After"	"Before"	"After"	"Before"	"After"
Quantity adsorbed	mmol/g	0.082	0.104	0.031	0.025	0.032	0.036	0.027	0.027
BET surface area	m ² /g	1.14	0.86	0.41	0.28	0.38	0.41	0.33	0.29
Langmuir surface area	m ² /g	2.38	1.62	0.73	0.43	0.71	0.98	0.72	0.63
BJH adsorption surface area	m ² /g	1.14	0.76	0.36	0.13	0.41	0.43	0.22	0.31
BJH desorption surface area	m ² /g	1.71	1.40	0.39	0.17	0.35	0.41	0.35	0.31
BJH adsorption total pore volume	10 ⁻³ cm ³ /g	2.86	3.59	1.03	0.76	1.09	1.21	0.84	0.90
BJH desorption total pore volume	10 ⁻³ cm ³ /g	2.89	3.65	1.08	0.83	1.13	1.20	0.93	0.93
BET adsorption average pore diameter	nm	5.0	5.7	5.2	5.0	4.7	5.1	4.7	6.2
BJH adsorption average pore radius	nm	5.0	9.4	5.8	12.1	5.3	5.6	7.4	5.7
BJH desorption average pore radius	nm	3.4	5.2	5.6	9.6	6.5	5.8	5.4	6.1

5.2. The Repeatability of Determining the Values of the Effective Diffusion Coefficients

The studies into the repeatability of determining the values of the effective diffusion coefficients were conducted on the basis of the analysis of the courses presented in Figure 5. The values of the effective diffusion coefficients D_e were determined from Formula (4), based on the courses of the saturation of samples with methane under the pressure of 1 bar. Table 5 presents the results of the repeatability of determining the values of the effective diffusion coefficients, together with the statistical analysis and measurement uncertainties. In the consecutive columns of Table 5, the following entities can be found:

1. Sample no.
- 2–4. $D_{e1}, D_{e2}, D_{e3} \left[\frac{\text{cm}^2}{\text{s}} \right]$ —the values of the effective diffusion coefficients determined in the 1st, 2nd, and 3rd measurement series,
5. $\overline{D_e} \left[\frac{\text{cm}^2}{\text{s}} \right]$ —the mean value of the effective diffusion coefficient obtained from the three-measurement series, calculated from the formula:

$$\overline{D_e} = \frac{D_{e1} + D_{e2} + D_{e3}}{3},$$

6. $x_{D_e} \left[\frac{\text{cm}^3}{\text{g}} \right]$ —the mean uncertainty of determining the value of the diffusion coefficient from three measurement series, calculated from the formula [33]:

$$x_{D_e} = \frac{|D_{e1} - \overline{D_e}| + |D_{e2} - \overline{D_e}| + |D_{e3} - \overline{D_e}|}{3},$$

7. $\frac{x_{D_e}}{\overline{D_e}} \cdot 100\% [\%]$ —the relative mean uncertainty.

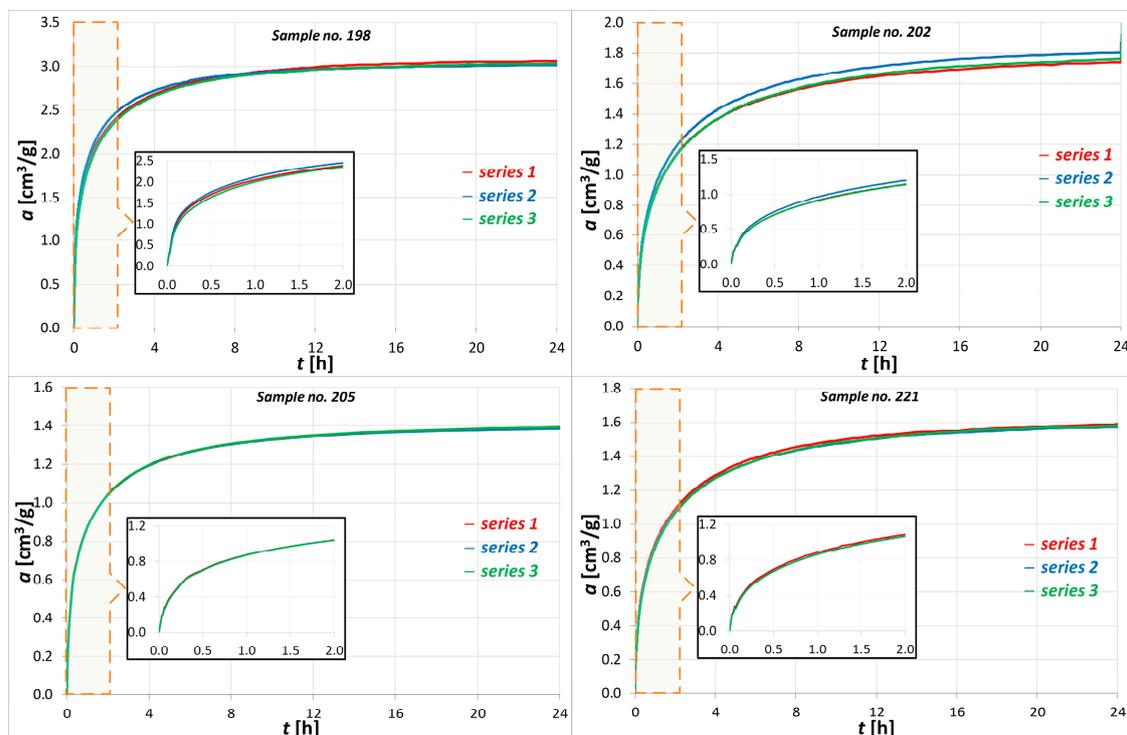


Figure 5. The compilation of the courses of threefold saturation of coal samples with methane under the pressure of 1 bar (a fragment of the saturation process from Figure 3).

Table 5. The results of the repeatability of determining the values of the effective diffusion coefficients obtained with the IGA-001 instruments, for a threefold measurement cycle.

1	2	3	4	5	6	7
Sample no.	Series 1	Series 2	Series 3	Mean	Mean uncertainty	Relative uncertainty
	D_{e_1} $[10^{-9} \cdot \frac{\text{cm}^2}{\text{s}}]$	D_{e_2} $[10^{-9} \cdot \frac{\text{cm}^2}{\text{s}}]$	D_{e_3} $[10^{-9} \cdot \frac{\text{cm}^2}{\text{s}}]$	$\overline{D_e}$ $[10^{-9} \cdot \frac{\text{cm}^2}{\text{s}}]$	x_{D_e} $[10^{-9} \cdot \frac{\text{cm}^2}{\text{s}}]$	$\frac{x_{D_e}}{\overline{D_e}} \cdot 100\%$ [%]
198	2.92	3.45	2.64	3.01	0.299	9.94
202	0.91	0.80	0.69	0.80	0.075	9.37
205	2.11	2.07	2.12	2.10	0.020	0.94
221	1.32	1.18	1.23	1.24	0.051	4.09

The discrepancies in determining the values of the effective diffusion coefficients by means of the IGA-001 instrument, for the measurement series repeated three times, were no greater than 10% in relation to the mean value.

Some of the assumptions concerning the boundary conditions [14] for which solution (3) holds true, are difficult to fulfill, and in some cases—impossible to fulfill. As one of the assumptions specifies, the sorption process occurs in accordance with Henry’s linear isotherm (2). Thus, the values of the effective diffusion coefficients in the conducted research were determined for the saturation pressure of 1 bar.

Another assumption of the solution of the unipore diffusion model states that the sorption process occurs in a seam composed of identical, spherical grains. In the research, granular samples of comminuted hard coal were used. The shape of the samples was not spherical. Therefore, the application of Formulas (3) and (4) gives us the results that are correlated only with the searched coefficient D_e . The degree of correlation depends on the deviations between the shape of the actual grain and sphere. If the shape of the grains in the coal samples used in the comparative studies can be regarded as statistically close to a sphere, the results of the application of Formulas (3) and (4) can be compared. The samples destined for comparative measurements were obtained in the course of dividing a bigger sample of the granulated material into three portions. Therefore, we can assume that the shapes of grains in each portion are statistically similar.

Another assumption that is difficult to fulfill is a sudden change of the concentration (pressure) of gas surrounding the grain in time $t = 0$, which is to initiate the processes of gas transportation within the porous structure of the sorbent. This assumption can be fulfilled only partially. The speed with which the sorption process occurs can be described with the exponent of Formula (3), equalling $W = \frac{D_e \cdot \pi^2}{R_0^2} \left[\frac{1}{\text{s}} \right]$. The initial change of pressure around the grains happens in time $t^* > 0$. The closer the product $W \cdot t^*$ is to zero, the better the assumption concerning the “sudden” pressure change is fulfilled.

For the grain fraction of the samples used in the research (0.20–0.25 mm) and the changeability of the values of the effective diffusion coefficients within the range $D_e = 10^{-10} - 10^{-8} \frac{\text{cm}^2}{\text{s}}$, typical of the coals from the Upper Silesian Coal Basin in Poland, the discrepancies in the repeatability of the results of ca. 10% are—in the authors’ opinion—to be accepted.

6. Conclusions

The research described in the present paper was to investigate the repeatability of the sorption processes occurring in the coal-methane system for a multiple measurement series. The objects of comparison were both sorption capacities and the values of the effective diffusion coefficients. The obtained results showed that both the sorption capacities of coal and the values of the effective diffusion coefficients do not change in the monotonic manner as a result of a threefold repetition of the sorption-desorption cycle. Thus, hypotheses stating that the sorption parameters of coal change with consecutive cycles of saturating coal with a sorbing gas were not confirmed. The presence of

such a phenomenon was suggested, among others, by [8], who attributed the changes in the sorption parameters to the sorptive swelling of coal, resulting in enlargement of the sorption area.

Sorption processes are divided into adsorption (occurring on the surface of the sorbent) and absorption (penetration into the coal matrix) [34]. Sorption processes bring about swelling of the coal and desorption processes its shrinking [35]. In the sorption experiments carried out, changes in the coal volume were not recorded. However, the achieved results may suggest that the reversibility of the sorption/desorption process results in the reversibility of the swelling/shrinking process of coal.

The research into the repeatability of the measurements of sorption capacities, conducted with the IGA-001 gravimetric device, showed that the obtained measurement discrepancies, in relation to the mean value, were no greater than 1.23% (Table 3). The discrepancies approximated the measurement uncertainty of the IGA-001 instrument.

On the basis of the volumetric measurements of the low-pressure adsorption (0–1 bar, 77 K) with nitrogen serving as the adsorbate ($0 \leq p/p_0 \leq 1$), the pore structure of the coal materials before and after saturating them with CH₄ during a triple repetition cycle was described. As a result of the nitrogen adsorption, the isotherms of type IV were obtained. Additionally, in samples 198 (“Before” and “After”), hysteresis loops were observed, undetected in the remaining samples. In all the samples, distribution of the pores before and after saturating them with CH₄ had a very similar course and similar values, which proves that the process of saturation has no impact on the pore structure of the samples.

For samples 198 and 205, the values of the adsorbed quantity of N₂ and of the available surface area (BET, Langmuir, BJH) increased slightly after the process of saturating the coal material with CH₄, and decreased in the case of samples 202 and 221. The total volume of the pores and their average diameter did not alter considerably either.

In light of the very small differences in the values of the structural parameters, it was concluded that saturating the coal samples with CH₄ during a triple repetition cycle did not cause any changes in the pore structure of these samples.

In the case of sample 198, the obtained values of the structural parameters were higher. This was due to the different structure of coal 198, which came from a different mine.

The evaluation of the repeatability of the process of determining the effective diffusion coefficients showed that the obtained discrepancies were no greater than 10%, which could stem from the problems connected with fulfilling most the assumptions of the solution (3) to the unipore diffusion model, used in determining the values of the effective diffusion coefficients.

The research carried out showed that in the range of the tested pressure levels, the analysed coal was fully recyclable compared to methane.

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