

Article

Influence of Depth on CO₂/CH₄ Sorption Ratio in Deep Coal Seams

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Abstract: The present work aims to analyse the influence of present-day burial depths of coal seams on the sorption properties towards CH₄ and CO₂, respectively. For medium-rank coals located in the southwestern area of the Upper Silesian Coal Basin (USCB), the gravimetric sorption measurements were carried out with pure gases at a temperature of 30 °C. The variability of CO₂/CH₄ exchange sorption and diffusivity ratios was determined. It was revealed that in coal seams located at a depth above 700 m, for which the sorption exchange ratio was the greatest, the process of CO₂ injection for permanent storage was more beneficial. In the coal seams lying deeper than 700 m with a lower CO₂/CH₄ sorption ratio, the CH₄ displacement induced by the injection of CO₂ (CO₂-ECBM recovery) became more favourable.

Keywords: coal; depth; sorption capacity; diffusion coefficient; CO₂ storage; ECBM

1. Introduction

Greenhouse gases pose a threat to the climate and human living conditions on Earth [1]. Not only CO₂ is dangerous; so is CH₄, emitted by some branches of the mining industry, which has an impact on the greenhouse effect more than twenty times greater [2]. Effective CO₂ sequestration is an important aspect of climate change. The use of the exchange sorption process to reduce CO₂ emissions into the atmosphere, combined with sustainable economic practices, brings potential benefits to our planet and its inhabitants [3]. In terms of reducing CO₂ emissions, the International Energy Agency stated that in order to achieve a sustainable development scenario, the dynamics of carbon capture and storage and CCS processes should be increased from the current 40 Mt CO₂ per year to approximately 5.6 Gt CO₂ per year in 2050 [4]. Geologic sequestration, as a method of CO₂ neutralization, has for years been a difficult issue for researchers looking for an effective implementation of the process; hence, it has its supporters and opponents. Undoubtedly, the geologically complex nature of the rock mass poses obstacles for the selection of appropriate reservoirs where CO₂ storage would be effective and irreversible. Among promising areas for the implementation of CO₂ storage technology are coal seams, which originally contain sorbed methane, but for economic reasons, the exploitation of coal from such seams is not profitable. The ability of coal to sorb CH₄ and CO₂ is the basic mechanism enabling the storage of both gases. Sequestration of CO₂ involves sorption exchange between CH₄ bound in the porous structure of coal and CO₂ injected into an unmineable coal seam. Due to their properties, CO₂ molecules have a greater affinity to coal; thus, they firstly displace and then replace coalbed methane (CBM) molecules contained in the seam. As a result of the CO₂/CH₄ exchange, CBM may be captured and used for energy purposes [5–9]. This method of eliminating the unfavourable impact of CO₂ on the environment is called enhanced coalbed methane recovery, or CO₂-ECBM [10,11]. Despite sceptical reviews after field tests of the RECOPOL project, geological CO₂ storage was found to be one of the most promising methods of CO₂ utilization from stationary sources [12].

The characteristics of coal seam occurrence in terms of burial depth are important indicators for determining the CO₂ sequestration potential [13]. It was determined that



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the suitable geological conditions for this process include depths from 300 to 1300 m. Laboratory data on the variability of the CO_2/CH_4 exchange ratio, together with data on the actual depth of the seams, are limited. As the depth of coal seams increases, changes occur in the sorption properties of coal, such as sorption capacity and sorption kinetics, described by the effective diffusion coefficient [14]. Assessment of the effectiveness of the sorption exchange process in seams located at different depths requires carrying out coal sorption tests in relation to changes in the degree of coalification [15]. Due to a close correlation with the depth of the seam, the degree of coalification of the coal substance is the main factor influencing the sorption properties of coal towards CH_4 and CO_2 . Therefore, in order to take into account issues related to the use of unmineable deep coal seams for CO_2 immobilization techniques, it is necessary to study the sorption capacity and kinetics of coal seams with various degrees of coalification. This will allow for the differentiation of the sequestration potential of coal seams as well as the identification of those that are more promising for CO_2 -ECBM. Continuing research on the possibility of geological storage of CO_2 is an important step for environmental protection and sustainable development.

Isotherm data are important for the balance of sorption exchange, i.e., assessing the amount of CH_4 that will be obtained by desorption and assessing the amount of CO_2 that can be located in the seam [5,16]. Research by the author and other researchers showed a reduction in the sorption capacity of carbon in relation to CH_4 [17]. Both in the case of sorption capacity and the effective diffusion coefficient, the dominant factor influencing the nature of the variability of the mentioned parameters with depth was the degree of coalification [17–19]. In the depth range from approximately 680 m to 860 m, the impact of temperature sorption properties was small compared to the coalification degree of the coal substance. Laboratory tests and literature reviews have shown that CO_2 sorption is approximately twice as high as CH_4 sorption [20]. As a result, twice as much CO_2 can be stored in the coal seam, in exchange for CH_4 desorbing from coal. For some degrees of coalification, the CO_2/CH_4 ratio can be much higher than two [7].

Some researchers also reported that the CO_2/CH_4 sorption ratio decreased with the coalification degree increase [13,21]. It was also shown, by examining the CO_2/CH_4 sorption efficiency, that a higher coalification degree resulted in an increase in the CH_4 displacement rate at low pressures [22]. As the sorption exchange ratio was influenced by the degree of coalification, it can also be affected by different seam depths. Due to the different geology of the basins, the burial depth will determine the possibilities of exchange sorption in coal seams. Moreover, it is expected that deeper coal seams will have better sorption properties for CH_4 displacement in the CO_2 -ECBM process due to the lower CO_2/CH_4 ratio.

The hypothesis raised here states that coal seams lying deeper in the strata have sorption properties and the CO_2/CH_4 sorption exchange ratio that, as a result of CO_2 injection, predispose them to CBM production rather than CO_2 storage. The novelty of the research presented in this work consists in analysis of the sorption properties, capacity and kinetics, in relation to the actual depths provided by the mine services. The vertical axis analysis of the sorption characteristics of the seams is extremely important in relation to the CH_4/CO_2 sorption exchange processes and the assessment of the potential of the designed technologies.

The main aim of the present work is to determine the effect of depth on the suitability of coal seams from the southwestern USCB for CO_2 sequestration, with or without CH_4 recovery. The influence of geological factors, such as the degree of coalification, on the sorption exchange process is analysed to assess the effectiveness of CO_2 storage in unmineable coal seams or obtaining green fuel in the form of coalbed methane (CBM).

2. Materials and Methods

2.1. Samples

The twelve coal samples were selected to represent coal seams deposited successively according to the stratigraphic systematics at different depths [17]. The samples were

collected before 2021 from a high-methane mine placed in the southwestern zone of the Upper Silesian Coal Basin. The coal seams belong to two tectonically separated zones of the coal mine, E and F (Figure 1). Within the particular zones, deeper depleted coal seams were characterised by greater degrees of coalification.

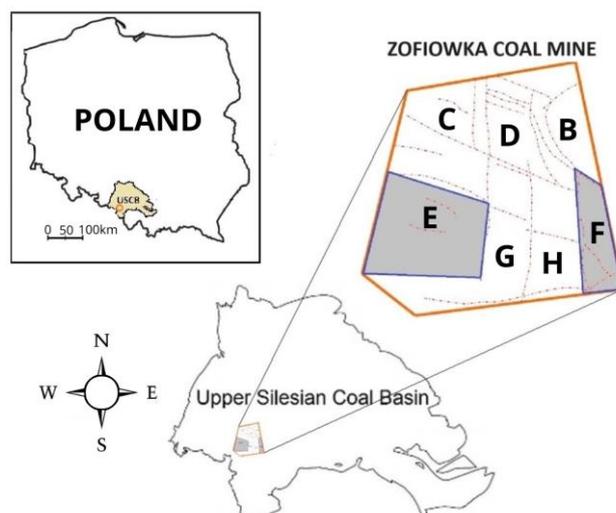


Figure 1. Location of the sampling sites in zones E and F of the Zofiówka mine.

The coal material was taken from the side walls of the coal seam excavations. Coal samples were secured in closed containers, transported to the laboratory and subjected to mechanical processing to obtain appropriately crushed material. Table 1 contains the basic characteristics of the samples—volatile matter (V^{daf}), ash (A^a) and moisture contents (W^a) as well as values of vitrinite reflectance, R_o . The petrographic composition of the studied coals can be accessed in previous work, e.g., [17]. The R_o value was closely correlated with the degree of coalification of the carbonaceous substance. According to Table 1, vitrinite reflectance increased approximately linearly with the increase in the average depth of deposition. It was consistent with the fact that the degree of coalification is governed by Hilt's law [23]. The study assumed that the samples taken from the Zofiówka mine represented technical, sorption and maturity properties of the subsequent coal seams from which they were collected.

Table 1. Coal samples obtained from the studied seams of Zofiówka coal mine.

Sample/ Coal Seam	Zone	d [m]	R_o [%]	ρ_r [g/cm ³]	V^{daf} [%]	A^a [%]	W^a [%]
404/2	F	696	1.01	1.370	25.29	5.01	2.09
404/4		733	0.98	1.338	24.78	6.00	1.84
405/1		771	1.04	1.389	20.58	11.57	1.19
405/2		825	1.01	1.465	22.33	15.68	1.16
406		828	1.05	1.435	27.84	2.58	1.95
407		863	1.11	1.373	23.25	6.31	1.13
410		E	678	1.10	1.344	20.79	7.54
412	716		1.07	1.356	19.42	11.77	1.39
413	794		1.14	1.313	18.35	3.49	1.31
416	799		1.13	1.372	19.17	9.57	1.00
418	825		1.16	1.407	16.54	8.02	1.32
502	859		1.25	1.380	13.82	6.48	1.15

Note: F, E—designation of the coal mine zones; d —average depth of coal seam; R_o —vitrinite reflectance; ρ_r —real density; V^{daf} —volatile matter yield with dry-ash-free basis; A^a —ash yield with dry basis; W^a —moisture content on air-dried basis.

According to Table 1, average burial depths of the Zone E coal seams ranged from 678 to 859 m, while the Zone F coal seams were depleted at an average depth from 696 to 863 m. The average vitrinite reflectance of coals covered the R_o value from 0.98% to 1.1% (Zone E), while for samples belonging to Zone F, the R_o range included values from 1.01% to 1.25%. According to the UN-ECE classification, all tested coals were classified as medium-rank coals [24].

2.2. Sorption Measurements

It was assumed in the work that the sorption capacity of coal (a) was responsible for the accumulative sorption properties of coal seams towards CH_4 and CO_2 . Sorption capacity determined the amount of gas that could be deposited in coal under specific pressure and temperature conditions. The sorption capacity was expressed in cm^3/g (dry ash-free basis). Kinetic sorption properties related to the accumulation rate of CH_4 and CO_2 were represented by the effective diffusion coefficient (D_e) expressed in cm^2/s .

2.2.1. Determination of Isotherms

CH_4 and CO_2 sorption tests were carried out using the IGA-001 gravimetric sorption analyser (Hiden Isochema, Warrington, UK). In order to ensure an appropriate time frame for sorption measurements in the atmosphere of single gases for 12 samples, which required establishing sorption equilibria for pressure points, the procedure below was adopted. Measurements with CH_4 were carried out on coal samples with a grain size of $0.125 \div 0.160$ mm and with a 12 h degassing and the same time waiting for sorption equilibrium. In measurements with CO_2 , which sorbs on coal much faster and in larger quantities, samples crushed to a grain size of 0.160–0.250 mm were used with 24 h degassing and equilibrium waiting time. Degassing was carried out on dry coal material at a temperature of 80°C in a high vacuum of 10^{-9} mbar.

Sorption measurements with CH_4 and CO_2 were performed on ca. 0.5 g of coal sample at a constant temperature of 30°C , below the critical conditions of CO_2 . The justification for choosing such a temperature was that the average deposit temperatures of the studied coal seams were not less than 30°C . Changes in the mass of coal samples under the influence of gas sorption were determined for the following sorption equilibrium pressures of methane: 1.0, 3.0 and 10.0 bar, and the following of carbon dioxide: 1.0, 5.0 and 12.0 bar. On the basis of sorption equilibria, the sorption capacity of the coal was determined based on standard conditions of pressure and temperature (*STP*). CH_4 and CO_2 sorption isotherms were determined using the approximation of sorption capacities using the Langmuir model in the form of the equation [25]:

$$a(p, T) = a_m \frac{p}{P_L + p} \quad (1)$$

where: a —sorbed amount of gas, $\text{m}^3\text{CH}_4/\text{g}$, a_m —maximum amount of gas sorbed by coal at pressure reaching ∞ (Langmuir volume), $\text{m}^3\text{CH}_4/\text{g}$, p —gas equilibrium pressure, bar, T —temperature, $^\circ\text{C}$, and P_L —pressure at which half of the a_m was sorbed (Langmuir pressure), bar.

Langmuir constants a_m and P_L provide important information on the sorption isotherm course and the sorption properties of the sorbent. The a_m constant determines the maximum sorption capacity of coal at a given temperature in the case of gas pressure in the system reaching its maximum value. Then, the amount of sorption sites is finite and determines the capacity of the monolayer. Langmuir pressure, P_L , is the value of the equilibrium pressure at which half of the maximum sorption capacity of coal is occupied by the sorbing gas molecules ($0.5 a_m$). The lower the P_L value, the greater the amount of gas sorbed at low equilibrium pressures.

2.2.2. Sorption Kinetics

During the sorption measurements with CH₄ and CO₂, a kinetic curve was recorded. For sorption obtained at a pressure of 1.0 bar, a detailed analysis of the registered kinetic curve was performed. It concerned the determination of the sorption half-time ($t_{0.5}$) and the value of the effective diffusion coefficient (D_e) for each of the tested coals. In order to estimate the diffusion coefficient, models based on the description of the pore structure of coal were used: the unipore [26–29] or bidisperse [30–32]. The most frequently used physical model is the unipore, referring to Fick's second law. After taking into account the linear Henry's equation and the equivalent (effective) diffusion coefficient $D_e = \frac{D}{1+K_H} \frac{\varepsilon}{k^2}$ [26], the sorption model can be written as Equation (2):

$$\frac{\partial c(r, t)}{\partial t} = \frac{D}{1 + K_H} \frac{\varepsilon}{k^2} \nabla^2 c(r, t) = D_e \nabla^2 c(r, t) \quad (2)$$

where:

D_e —effective diffusion coefficient, m²/s,
 K_H —Henry isotherm coefficient, m³/(g·bar),
 ε —porosity, -,
 k —coefficient characterizing the porous structure, -,
 r —distance from the centre of the grain, m.

In order to solve Equation (2), it was necessary to make many assumptions [27], including the homogeneity of the sorbent, the microporosity of the coal structure, the spherical shape of the grain, the isothermal sorption process, the gas filtration between sorbent grains, etc. Additionally, the transport of gas molecules through coal had to be described as a combination of several types of diffusion taking place in the diverse pore system of the sorbent. Diffusion was driven by the concentration gradient of the deposited gas molecules.

The solution of the unipore model for sorption was the following formula [26,27]:

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

where:

γ_{SOR} —the relative amount of sorbed gas, -,
 $a(t)$ —the gas content diffused at time t , cm³/g,
 a_{∞} —the total gas content sorbed on coal at equilibrium pressure, cm³/g,
 R —equivalent grain radius for a sample with grain diameters from d_1 to d_2 ,
 n —the n th level of the series.

The equivalent radius was calculated from Equation (3):

$$R = \frac{1}{2} \sqrt[3]{\frac{2 \cdot d_1^2 \cdot d_2^2}{d_1 + d_2}} \text{ [cm]} \quad (4)$$

Equation (3) makes it possible to determine the value of the effective diffusion coefficient D_e by measuring the amount of absorbed gas a , while ensuring isothermal and isobaric conditions of the process, at the pressure range corresponding to the straight-line section of the isotherm (saturation from vacuum to 1.0 bar gas pressure). The value of the effective diffusion coefficient was obtained using Timofeev's formula for time t , in which the amount of gas sorbed is half of the final amount ($\gamma = 0.5$):

$$D_e = \frac{0.308 R^2}{\pi^2 t_{0.5}} \quad (5)$$

where:

$t_{0.5}$ —sorption half-time, s.

3. Results

3.1. Accumulation Properties in Relation to CH_4 and CO_2

The results of gravimetric sorption measurements are presented for individual zones in the form of sorption kinetics in Figures 2 and 3 for CH_4 and in Figures 4 and 5 for CO_2 . As can be seen from the figures, different amounts of gas sorbed were recorded for specific pressure levels at sorption equilibrium. The saturation curves show that the amounts of sorbed CO_2 were greater in relation to the amount of sorbed CH_4 . Additionally, saturation time was longer in the case of CH_4 . All the curves show differences in the amount of sorbed gas and in the length of saturation time within samples belonging to a given zone. The arrangement of the curves suggest the variability trends of the sorption properties of coal, accumulation and kinetic, seen in individual zones. The CH_4 sorption isotherms, determined by approximation with the Langmuir model, are shown in Figures 6 and 7 for Zone E and Zone F coals, respectively. Similarly, the CO_2 Langmuir sorption isotherms are shown in Figures 8 and 9 for Zone E and Zone F coals, respectively.

If we compare the isotherm courses from Figures 6–9, which enable a quantitative description of the sorption process, it may be seen that the sorption capacity of coals in relation to both studied gases varies for particular seams within a given zone. In the case of CH_4 isotherms, the greatest sorption capacity among coals in Zone E was observed for the 410 sample, just before sample 412. These two samples were located at the shallow depths in Zone E and had the lowest R_0 values, 1.10% and 1.07%, respectively. However, sample 502 was characterised by the smallest sorption capacity, and it was located at the greatest depth in Zone E, representing the highest R_0 value, amounting to 1.25%. For coals taken from Zone F, the situation was similar. Sample 404/4 had the greatest sorption capacity with the lowest R_0 value, of 0.98%, while sample 407 had the smallest CH_4 sorption with the highest R_0 value among samples from Zone F, which was 1.11%.

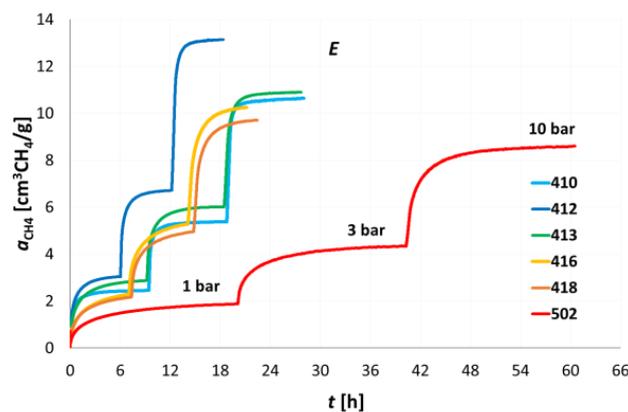


Figure 2. Kinetics of CH_4 saturation for Zone E coals at 1.0, 3.0 and 10.0 bar pressure levels.

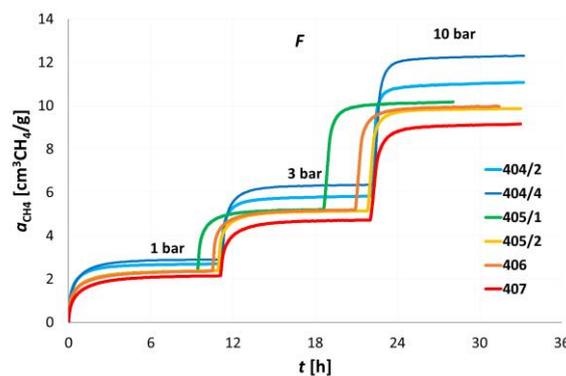


Figure 3. Kinetics of CH_4 saturation for Zone F coals at 1.0, 3.0 and 10.0 bar pressure levels.

Looking at the CO₂ isotherms, it can be seen that the greatest sorption capacity in Zone E was for sample 412 with the lowest R_o value among the tested seams, amounting to 1.07%. However, the smallest sorption capacity for CO₂, as in the case of CH₄, was possessed by sample 502, located at the greatest depth in the zone and representing the highest R_o value. In Zone F, sample 404/4 had the greatest sorption capacity, with a R_o of 1.01%, while the smallest CO₂ sorption was demonstrated by 406 and 407 coal samples, which both had the highest R_o among the seams in the zone.

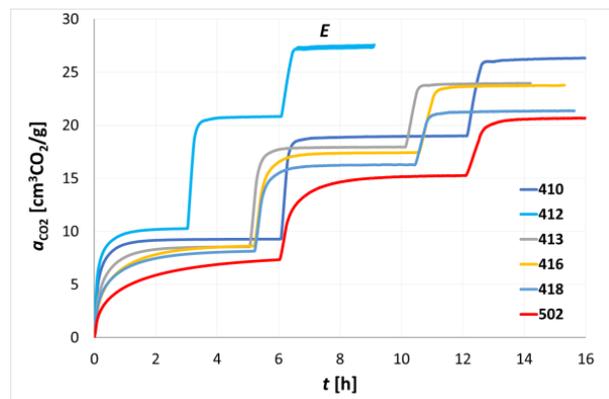


Figure 4. Kinetics of CO₂ saturation for Zone E coals at 1.0, 5.0 and 12.0 bar pressure levels.

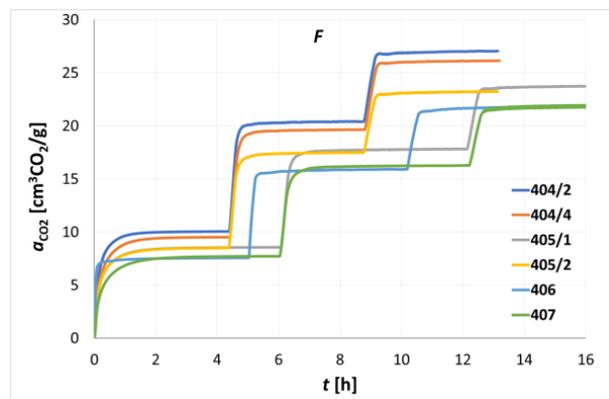


Figure 5. Kinetics of CO₂ saturation for Zone F coals at 1.0, 5.0 and 12.0 bar pressure levels.

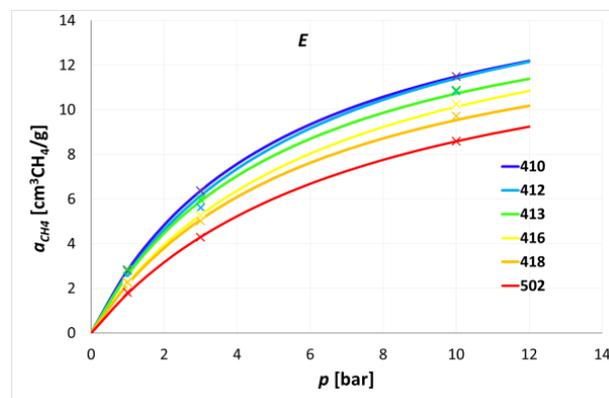


Figure 6. CH₄ sorption isotherms at 30 °C for Zone E coals.

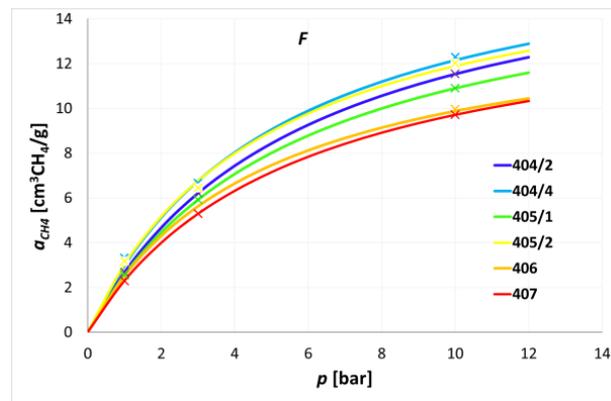


Figure 7. CH₄ sorption isotherms at 30 °C for Zone F coals.

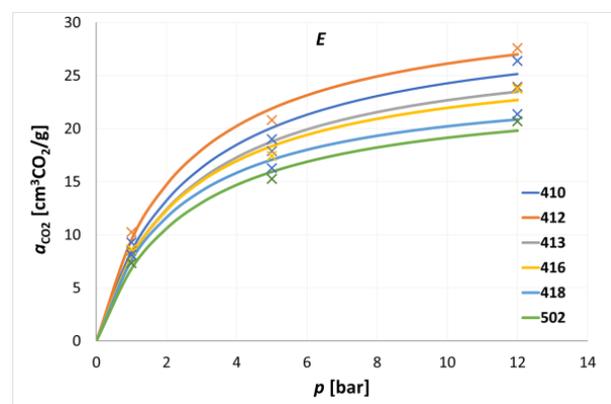


Figure 8. CO₂ sorption isotherms at 30 °C for Zone E coals.

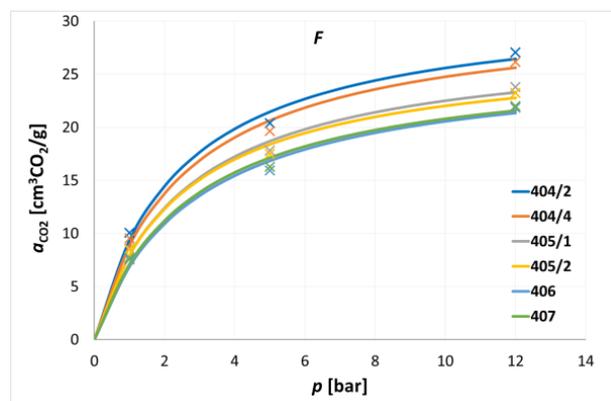


Figure 9. CO₂ sorption isotherms at 30 °C for Zone F coals.

CH₄ and CO₂ Sorption Isotherms Analysis

The obtained values of the Langmuir parameter for all coal samples and both tested gases are listed in Table 2. As can be seen, the maximum sorption capacity of coal a_m as well as the half-sorption pressure P_L showed variability trends within particular zones and both in relation to CH₄ and in relation to CO₂.

Table 2. Langmuir parameters for CH₄ and CO₂ sorption isotherms at 30 °C.

Coal Seam	Zone	$a_m(\text{CH}_4)$ [cm ³ CH ₄ /g]	$P_L(\text{CH}_4)$ [bar]	$a_m(\text{CO}_2)$ [cm ³ CO ₂ /g]	$P_L(\text{CO}_2)$ [bar]
404/2	F	18.25	5.81	31.71	2.39
404/4		18.47	5.21	30.93	2.50
405/1		17.06	5.65	28.26	2.56
405/2		17.64	4.83	27.44	2.46
406		15.14	5.59	24.14	2.84
407		14.64	5.46	22.17	2.72
410		17.53	5.26	30.69	2.64
412	E	18.05	5.81	32.41	2.40
413		16.49	5.38	28.57	2.61
416		16.68	6.45	27.33	2.44
418		15.31	6.06	24.80	2.26
502		14.98	7.44	24.00	2.53

Note: F, E—designation of the coal mine zones.

The impact of changes in the coalification degree of coal seams on the maximum sorption capacity in relation to CH₄ is shown in Figure 10. As may be seen, with the increase in vitrinite reflectance the maximum sorption capacity of coal decreased. The relative reduction of the $a_{m\text{CH}_4}$ value with R_o was greater in the case of Zone F coals (by 3.6 cm³/g, which led to a ca. 20% reduction in $a_{m\text{CH}_4}$ for every increase in R_o by 0.1%) compared to Zone E coals (by 1.7 cm³/g, which led to a 10% reduction in $a_{m\text{CH}_4}$ for every increase in R_o by 0.1%). By converting the obtained reductions into the variability of CH₄ sorption with depth of the seam deposition, a consistent conclusion can be drawn for both studied zones, that the maximum sorption capacity of coal in relation to CH₄ decreased by 2.2 cm³/g due to an increase in the seam depth of 100 m (see also Tables 1 and 2).

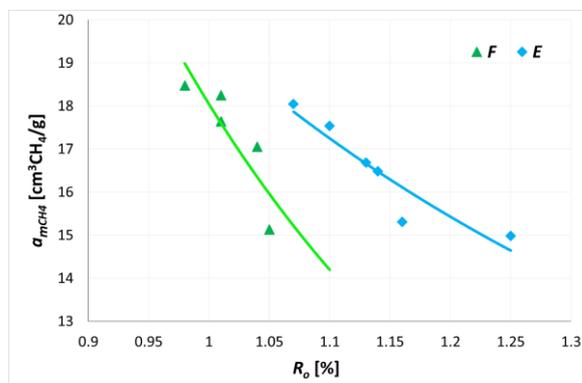


Figure 10. The influence of the coalification degree of Zone E and Zone F coals on the maximum sorption capacity towards CH₄.

Similarly, Figure 11 shows the influence of the coalification degree on the maximum sorption capacity of coal in relation to CO₂. The obtained trends were similar to those observed during the analysis of sorption results towards CH₄. As the reflectance R_o increased, the maximum sorption capacity of coal decreased (see Figure 11). The relative reduction in $a_{m\text{CO}_2}$ value with R_o was greater in the case of Zone F (by 9.7 cm³/g, giving a 31% reduction in $a_{m\text{CO}_2}$ for every 0.1% increase in R_o) compared to Zone E coals (by 4.5 cm³/g, giving a 15% reduction in $a_{m\text{CO}_2}$ for every increase in R_o by 0.1%). By converting the obtained reductions into the variability of CO₂ sorption with depth of seam deposition, another conclusion can be drawn for both tested zones, that the maximum sorption capacity of a coal seam in relation to CO₂ decreased by 5.0 cm³/g as a result of an increase in the deposition depth by 100 m (see also Tables 1 and 2).

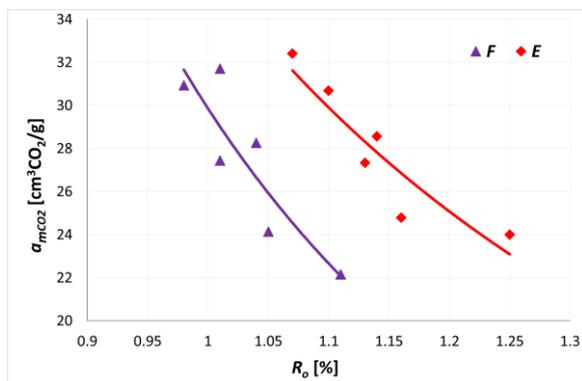


Figure 11. The influence of the coalification degree of Zone E and Zone F coals on the maximum sorption capacity towards CO₂.

As may be seen in Figures 12 and 13, slightly different trends were represented by CH₄ and CO₂ Langmuir pressure in relation to vitrinite reflectance, R_o. According to the trends, the half-sorption pressure increased with degree of coalification; however, the P_L pressure level for CH₄ was more than twice as high as for CO₂. This was consistent with literature reports and the fact that CO₂ was preferentially sorbed by coal over CH₄. Thus, the filling of the sorbent with CO₂ in an amount corresponding to half of the maximum sorption capacity required half the pressure [33].

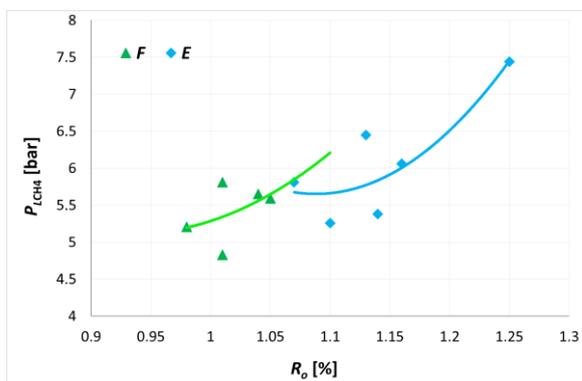


Figure 12. The influence of the coalification degree on the CH₄ Langmuir pressure for Zone E and Zone F coals.

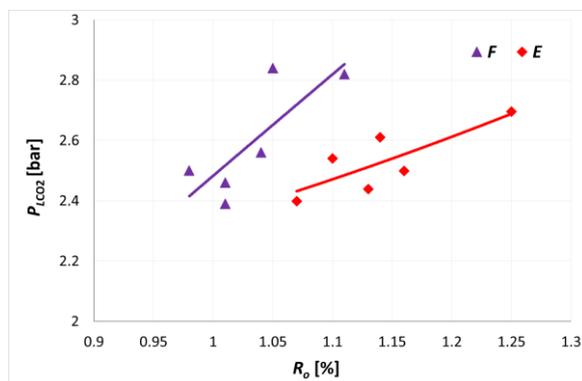


Figure 13. The influence of the coalification degree on the CO₂ Langmuir pressure for Zone E and Zone F coals.

3.2. Kinetic Properties in Relation to CH₄ and CO₂

According to Figures 2–5, the time needed to saturate coal samples with gas varied within coal seams belonging to a given zone. Table 3 shows the sorption half-time $t_{0.5}$ and the values of the effective diffusion coefficient of CH₄ (D_{eCH_4}) and CO₂ (D_{eCO_2}) determined at a temperature of 30 °C. According to Table 3, the CH₄ sorption half-time $t_{0.5(CH_4)}$ varied in the range from 625 s to 13,060 s. The values of the effective diffusion coefficient $D_{e(CH_4)}$, for the given half-times, corresponded to the variability range from 2.49×10^{-9} cm²/s to 1.19×10^{-10} cm²/s. For CO₂, the sorption half-time $t_{0.5(CO_2)}$ decreased from 360 to 2765 s, which corresponded with a reduction of the coefficient $D_{e(CO_2)}$ from 8.53×10^{-9} cm²/s to 1.11×10^{-09} cm²/s.

Table 3. Kinetic parameters of CH₄ and CO₂ sorption (30 °C).

Coal Sample	Zone	$t_{0.5(CH_4)}$ [s]	$D_{eCH_4} \cdot 10^{-09}$ [cm ² /s]	$t_{0.5(CO_2)}$ [s]	$D_{eCO_2} \cdot 10^{-09}$ [cm ² /s]
404/2		757	2.01	367	8.36
404/4		1105	1.41	475	6.46
405/1	F	1202	1.29	433	7.09
405/2		1153	1.35	446	6.88
406		1213	1.28	499	6.15
407		1669	0.93	591	5.19
410		625	2.49	360	8.53
412		1050	1.48	287	1.07
413	E	1035	1.50	622	4.94
416		2437	0.630	827	3.71
418		2468	0.629	833	3.69
502		13,060	0.119	2765	1.11

Note: F, E—designation of the coal mine zones.

According to Li et al. [34], the time needed to establish sorption equilibrium on coal with a low coalification degree was ten times shorter than that on highly coalified anthracite. The variability range of D_e obtained in this study, covering one order of magnitude, confirmed the occurrence of changes in the internal structure of coal depleted at different depths as a result of changes in the degree of coalification of the organic matter [35–37]. Changes in the deposit temperature of coal seams could have been neglected in work because, according to a study by Crosdale et al. [38], the degree of coalification had a much greater impact on sorption kinetics than temperature.

4. Discussion

4.1. The Influence of Depth on the Sorption Exchange CO₂/CH₄

As was shown above, together with an increase in the coalification degree, corresponding to different depths of coal seams, the sorption capacity of coal for CH₄ and CO₂ decreased. In the case of CH₄, the reduction in the maximum sorption capacity a_{mCH_4} was approximately 1.2% as the vitrinite reflectance increased by 0.1%. In the case of CO₂, similar reductions in the maximum sorption capacity were observed. An increase in the vitrinite reflectance by 0.1% resulted in a reduction of the a_{mCO_2} value by 1.5%. The obtained observations are in contradiction to those obtained by authors dealing with the influence of coal rank on the sorption capacity [13,39], who found that as the vitrinite reflectance increased, the ability of coal to adsorb CO₂ also increased. An explanation for such observations may be the example of studies carried out in relation to CH₄, which showed a falling and then rising trend [40]. In the range of vitrinite reflectance from 0.6 to 1.25%, there was a reduction in sorption capacity, while for $R_o > 1.3\%$ the trend changed to the opposite and the sorption capacity increased with the degree of maturity.

The obtained results in Section 3 are the basis for determining the possibility of sorption exchange between CH₄ and CO₂ in seams depleted at various depths. It is worth

emphasizing that, in the individual zones of the mine, coal seams were sampled according to stratigraphic order; thus, their coalification degree decreased linearly with depth.

4.1.1. CO₂/CH₄ Sorption Ratio

The possibility of sorption exchange of CH₄ for CO₂ in coal seams located at various depths was examined. The sorption ratio (SR) parameter was used, expressed as the ratio of the CO₂ maximum amount that can be stored in a coal seam to the maximum amount of CH₄ that can be displaced from it in the CO₂-ECBM process. In laboratory conditions, the sorption ratio SR was represented by the ratio of the maximum sorption capacities of coal in relation to CH₄ (*a_{mCH4}*) and CO₂ (*a_{mCO2}*). Table 4 compares the values of the SR parameter for CO₂/CH₄ sorption exchange in individual coal seams of the studied mine.

Table 4. Parameters of the sorption exchange of CH₄ for CO₂.

Coal Seam	$SR = \frac{a_{mCO_2}}{a_{mCH_4}} [-]$	$DR = \frac{D_{et(CO_2)}}{D_{et(CH_4)}} [-]$
404/2	1.74	4.17
404/4	1.67	4.58
405/1	1.66	5.49
405/2	1.56	5.11
406	1.59	4.80
407	1.51	5.58
410	1.75	3.43
412	1.80	7.23
413	1.73	3.29
416	1.64	5.82
418	1.62	5.87
502	1.60	9.34

The influence of the coalification degree on the CO₂/CH₄ ratio of sorption exchange for medium-rank coal seams is shown in Figure 14. As can be seen from Figure 14, in the case of seams belonging to Zone E, the greatest CO₂/CH₄ ratio, of 1.8, was obtained for the coal with the lowest reflectance, of 1.07%, while the smallest CO₂/CH₄ ratio, of 1.6, was obtained for coal with the highest reflectance, of 1.25%. In Zone F, the coal seam with the lowest vitrinite reflectance, of 1.01%, had the greatest CO₂/CH₄ sorption ratio, of 1.74, while the smallest CO₂/CH₄ sorption ratio, of 1.50, was for the coal seam with the highest vitrinite reflectance among the seams in that zone, *R_o* = 1.11%. The reductions in the CO₂/CH₄ exchange ratios obtained in both examined zones of the mine with the increase in coalification degree were the result of changes in the maximum sorption capacities of coal shown in Figures 10 and 11.

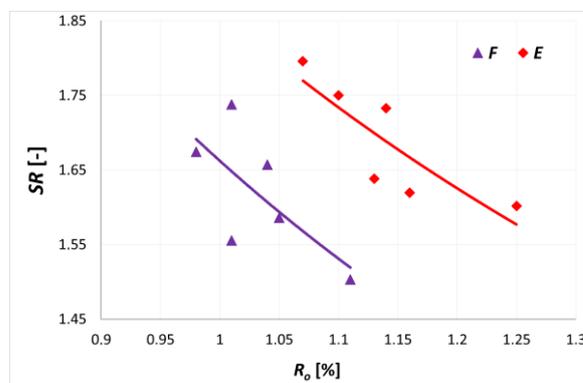


Figure 14. CO₂/CH₄ sorption ratio for coal seams from zones E and F with different degrees of coalification.

For both CH_4 and CO_2 , the a_m values decreased in the considered zones with an increase in the R_0 parameter. A greater value of the CO_2/CH_4 sorption exchange ratio suggested a better suitability of the coal seam for CO_2 storage, while a smaller value suggested better conditions for the intensification of CH_4 extraction from coal beds in CO_2 -ECBM.

Previous research has shown that coal rank is an important factor in determining this CO_2/CH_4 exchange ratio [41]. According to Garnier et al. [42], the sorption exchange factor of 1.4 for high-rank coals was compared to the factor of 2.2 for low-rank coals. The trend shown in Figure 14 confirms the qualitative variability of the CO_2/CH_4 ratio. In the specific case of the studied seams from coal mines in the southwestern zone of the Upper Silesian Coal Basin, the actual variability of the CO_2/CH_4 ratio parameter was obtained.

The analysis carried out above made it possible to identify coal seams intended for CO_2 sequestration purposes and coal seams with a greater potential for enhanced CH_4 recovery (Figure 15). In coal seams lying at depths <700 m, for which the sorption exchange ratio $SR = a_{m\text{CO}_2}/a_{m\text{CH}_4}$ was the greatest, the process of CO_2 injection for permanent storage in coal seams (CO_2 storage) was more promising. In deeper seams, lying at depths >700 m, for which the CO_2/CH_4 sorption ratio was smaller, the CH_4 production process intensified by the injection of CO_2 into the coal seams (CO_2 -ECBM process) became more important.

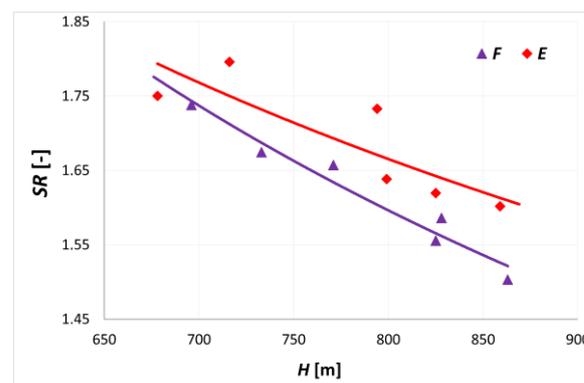


Figure 15. The influence of the seam depth on the CO_2/CH_4 sorption exchange ratio for zones E and F.

4.1.2. Kinetics of CO_2/CH_4 Sorption Exchange

As part of the discussion of the results, the CO_2/CH_4 sorption exchange rate was analysed. The diffusivity ratio (DR) was calculated by dividing the effective diffusion coefficients for CO_2 and CH_4 , respectively (see Table 4). Figure 16 shows the variability of DR with respect to depth of the seam. As may be seen from the trends, the increase in the diffusivity ratio of the CO_2/CH_4 was obtained in the deeper coal seams. The increase in the DR value in both zones by an average of 50% was a beneficial factor for the implementation of CO_2 injection into a coal seam with simultaneous CH_4 recovery. Despite the decrease in the rate of sorption processes with depth (see Table 3), the DR ratio indicated an increase in the rate of CO_2 sorption over CH_4 in the deeper coal seams. The greatest diffusivity ratio of sorption exchange was found in coal seam 502, Zone E, the deepest and of the greatest R_0 among the studied samples.

A few studies have shown that a higher degree of coalification resulted in a greater tendency to accelerate desorption of CH_4 from a coal seam with supercritical CO_2 , thereby enhancing CBM recovery [43]. Figure 16 again confirms the hypothesis that the sorption properties of deeper coal seams to favour the CH_4 recovery in the CO_2 -ECBM process over CO_2 sequestration.

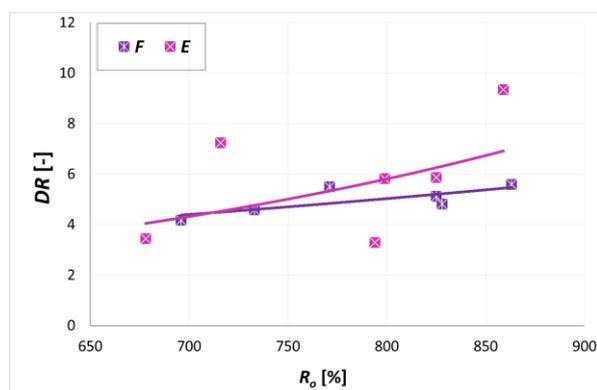


Figure 16. CO₂/CH₄ diffusivity ratio in zones E and F in relation to depth of coal seam.

5. Conclusions

Based on the conducted sorption studies on the influence of the degree of coalification and burial depth on the capacitive (a_m) and kinetic (D_e) properties of coal in relation to CH₄ and CO₂, the following conclusions could be drawn:

1. Sorption properties of the studied coal seams of the Zofiówka mine towards CH₄ and CO₂ were influenced by depth of the seam. The values of the maximum sorption capacity of the studied coal seams ranged from 14.637 to 18.474 [cm³/g] for CH₄ and from 22.167 to 32.410 [cm³/g] for CO₂ in a ca. 650–850 m depth range.
2. The increase in CH₄ and CO₂ Langmuir pressure with the increase in coalification degree indicated the need to inject the CO₂ into deeper coal seams at a higher pressures to obtain a similar sorption capacity as for the shallower seams.
3. The CO₂/CH₄ exchange ratio (SR) for the studied coal seams ranged from 1.51 to 1.8. Based on changes in SR value with burial depth, it was shown that the coal seams with a lower degree of coalification, which are located in particular zones at shallower depths, turned out to be promising for CO₂ storage purposes. In coal seams with a higher degree of coalification, the CO₂/CH₄ sorption ratio was smaller. As the depth of the seams increased, the enhanced CH₄ recovery process caused by the injection of CO₂ became more important (CO₂-ECBM process).
4. An increase in the diffusivity ratio (DR) induced by the increase in depth was shown. The greatest DR ratio was a favourable premise for implementing the CO₂-ECBM process, more than for CO₂ storage purposes alone.

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