

Impact of preparation and storage of activated carbon on the high pressure sorption of CO₂

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Abstract. Adsorption of carbon dioxide on activated carbons has become extremely interesting in the field of energy and environment. Activated carbon is either used as a model to understand sorption processes on coals as a part of research on CO₂ geological storage/Enhanced Coalbed Methane or as an adsorbent for processes such as natural gas treatment or CO₂ separation from flue gas. The paper presents results of high-pressure CO₂ sorption at the temperature of 318K on two similar activated carbons (Filtrisorb 400 and WAZ 0.6–2.4 mm) where one sample of WAZ was not subjected to any pretreatment procedure. Experimental results were fitted with three parameter Langmuir and therefore it was possible to calculate CO₂ adsorbed phase densities. The WAZ activated carbon has a slightly lower sorption even though it was pretreated with the same procedure. The untreated sample of WAZ exhibited sorption which was lower over 15%. Calculated adsorbed phase densities differ between the activated carbons and the lowest value was obtained for the untreated WAZ sample (21.0 mol/dm³).

Key words: activated carbon, sorption, carbon dioxide.

1. Introduction

Adsorption of carbon dioxide on activated carbons has become extremely interesting in the field of energy and environment where CO₂ emission reduction targets are a challenge for countries where fossil fuels are a dominant source of energy. Activated carbon is either used as a model to understand sorption processes on coals as a part of research on CO₂ geological storage/Enhanced Coalbed Methane or as an adsorbent for processes such as natural gas treatment e.g.: Pressure Swing Adsorption (PSA) method, Temperature Swing Adsorption (TSA) method, etc. These methods can be also used for the separation of CO₂ from flue gas as a carbon capture technology.

In recent years measurements of carbon dioxide sorption on both activated carbons and coals have been focused on accuracy of the sorption setup. Such studies were performed regarding coals [1–5] as well as activated carbons [6]. These studies reveal that the setup and the equation of state of high accuracy [7] are crucial for obtaining a reliable isotherm. Nevertheless, it is also important to properly prepare the sample used for the tests.

Typical activated carbon reactivation methods can be divided into chemical and thermal treatment methods. In case of chemical treatment the surface of activated carbon is modified by chemical impregnation which can significantly increase sorption capacity. The surface chemistry of activated carbon can be modified creating acidic or basic groups [8, 9]. Due to the acidic nature of CO₂ the higher sorption capacity is obtained when basic species are introduced to the surface [10]. One of the popular ways used for preparation of activated carbon with increased basicity is introducing nitrogen to the carbon structure. This can be performed by prepar-

ing activated carbon from N-containing polymers [11, 12] or treating activated carbon with ammonia. In the work of [13] it was observed that modification of activated carbon fiber (ACF) with dry ammonia at several temperatures from 500 to 800°C for different periods of time results in the formation of new nitrogen-containing groups in the structure of the fiber. Interesting result was obtained by [14] where the adsorption of CO₂ was significantly enhanced by ammonia treatment of the AC sample at temperature below and above 400°C. The enhancement is caused by the presence of C = N and C – N species involved in the structure of tested activated carbons. The CO₂ uptake was the largest at 400°C of the ammonia treatment temperature. In this study the adsorption was performed under very low pressure i.e. 0.125 MPa.

Impregnation by metal oxides such as Cr₂O and Fe₂O₃ showed an increase in sorption capacity by 15% [15]. Nevertheless, the most common method in case of CO₂ is thermal treatment i.e. drying at approximately 343–353 K [16, 17], 378–382 K [6, 18, 19]; or 433 K [20]. Other authors do not describe the detailed treatment or reactivation procedure of activated carbon e.g. [21].

The purpose of this paper is to present results of high-pressure CO₂ sorption at the temperature of 318 K on two similar activated carbons where one was not subjected to any pretreatment procedure. This may reveal to what extent thermal treatment of the activated carbon sample may have an impact on the total sorption capacity and the shape of an isotherm.

2. Materials

Two adsorbates were selected for the study, both were granulated activated carbons (GAC) made from the same material

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i.e. coal. The first one was WAZ 0.6–2.4 mm manufactured by Elbar Katowice [22], a granular activated carbon produced from coal by steam-gas technology. It combines the typical features in addition to coal qualities such as the highly developed surface area and high adsorption capacity, high resistance to abrasion and grain granulometry. The other was Filtrasorb 400 manufactured by Calgon Carbon [23], a granular activated carbon made from select grades of bituminous coals through a process known as reagglomeration to produce a high activity, durable, granular product capable of withstanding the abrasion associated with repeated backwashing, hydraulic transport and reactivation for reuse. Filtrasorb 400 is an adsorbent widely used for studies of supercritical adsorption of CO₂ [6, 16, 20, 24]. Specification and properties of the materials are presented in Table 1.

Table 1
Specification and properties of Filtrasorb 400 and WAZ 0.6–2.4 mm, source Refs. [22, 23]

Specification and properties	Filtrasorb 400	WAZ 0.6–2.4 mm
Iodine number	1000 mg/g (min)	1000 mg/g (min)
Surface area	1050 m ² /g	1050 m ² /g
Moisture	2 % (max)	5 % (max)
Effective size	0.55–0.75 mm	0.6–2.4 mm
Ash content	6.46 %	12% (max)
Bulk density	540 g/dm ³	420 g/dm ³

As it was mentioned in the previous paragraph, the purpose of the study was to assess to what extent the pretreatment of GAC can impact sorption capacity of CO₂ and to what extent activated carbon with similar properties (eg. iodine number, surface area) may have different sorption capacity. Major factor affecting sorption is the temperature therefore experiments were performed under the same sorption temperature i.e. 318 K. For the first experiment an untreated WAZ 0.6–2.4 mm was used. Although this activated carbon has never been used it was stored in a partially sealed bag exposed to the atmosphere in the laboratory and light for approximately 5 years. It was intentionally used for the experiments in order to see what is the impact of improper storage and preparation on sorption results. Before starting the actual sorption experiment, the WAZ activated carbon was only degassed under vacuum for 24 hours.

The second set of experiments involved thermal treatment of granulated activated carbons in an oven for 24 h at 373.15 K. Then, the samples were quickly transferred to the sample cell in order to avoid contact with air and degassed under vacuum for 24 h at the temperature of 318 K. The amount of untreated WAZ (WAZ-1) used for the measurement was 26.1 g and the same amount of dried WAZ (WAZ-2) was used.

The accuracy of experiments was verified by duplicating CO₂ sorption experiments on Filtrasorb 400 and comparing results with European inter-laboratory comparison of high pressure CO₂ sorption on activated carbon [6]. In this case

both samples of Filtrasorb 400 (Filtrasorb-1, Filtrasorb-2) had a weight of 32.3 g. The results were satisfactory and proved that the setup and experimental procedure is correct.

3. High pressure sorption measurements

3.1. Measuring methodology. Sorption experiments were performed using the manometric technique with custom made sample cells and setup. The process of adsorption removes sorbate gas molecules from the free gas phase and thus results in a decrease of the gas pressure within the experimental system. The most fundamental operational procedure to quantify gas adsorption is the Gibbs approach where the amount of adsorbed gas (n_{adsorbed}) is defined as the difference between the total amount of gas (n_{total}) presents in the system and the amount occupying the void volume (V_{void}), i.e. the volume not occupied by the solid sample. This latter quantity is calculated from the molar concentration (c_{gas}) in the gas phase which is obtained from an equation of state of the gas for the corresponding pressure and temperature conditions with the formula [25]:

$$\begin{aligned} n_{\text{sorbed}} &= n_{\text{total}} - c_{\text{gas}} \cdot V_{\text{void}} \\ &= n_{\text{total}} - c_{\text{gas}} (V_{\text{sample cell}} - V_{\text{sample}}). \end{aligned} \quad (1)$$

Prior to the start of the actual experiment void volume of the sample cell (V_{void}) must be measured. For this purpose a non-adsorptive gas (Helium) was used. The density of gas was calculated with McCarthy equation of state [26]. Multiplication of the void volume by the density of the gas ($V_{\text{void}} \cdot \rho^{CO_2}(T, P)$) gives the “non-sorption” reference mass, i.e. the amount of gas that would be accommodated in the measuring cell if no sorption occurred. Whereas, the excess sorption mass is the difference between the mass of gas that has been actually transferred into the measuring cell up to a given pressure step and the “non-sorption” reference mass:

$$m_{\text{excess}}^{CO_2} = m_{\text{transferred}}^{CO_2} - V_{\text{void}} \cdot \rho^{CO_2}(T, P). \quad (2)$$

Sorption measurement is done in consecutive steps and the mass of gas transferred from the reference cell into the sample cell at each step (N) can be calculated with the use of the following formula:

$$m_{\text{transferred}}^{CO_2} = \sum_{(i=1)}^N V_{\text{ref}} \cdot (\rho_i^{(f, CO_2)} - \rho_i^{(e, CO_2)}). \quad (3)$$

Superscripts in the equation i.e. f , CO₂ and e , CO₂ refer to the density of the gas in the filling phase (when the reference cell is not connected with the sample cell) and equilibrium phase (when the sample cell is connected with the sample cell and the pressure is equilibrated), respectively. Densities of CO₂ were calculated with the use of high-accurate Span&Wagner equation of state [27]. Due to the long equilibration time for CO₂ each sorption step took approximately 24 to 48 hours. Schematic diagram of the manometric sorption methodology is presented in Fig. 1.

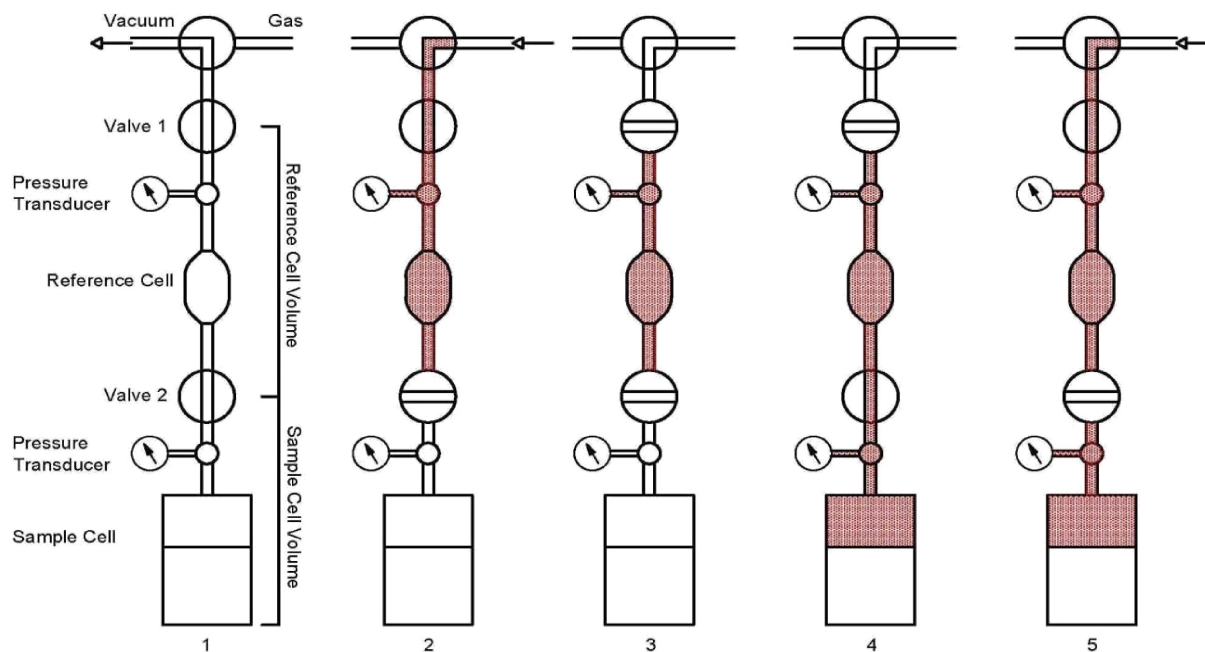


Fig. 1. Schematic diagram of the manometric sorption methodology, where each figure indicates each step: 1 – Evacuation of the system; 2 – Filling of the reference cell; 3 – Closure of the valve 1 and thermal equilibration; 4 – Valve 2 is opened and the gas is transferred into the sample cell; start of the sorption process; 5 – when pressure equilibrium is reached valve 2 is closed and refilling of the reference cell starts

3.2. Setup description. The manometric setup used for the experiments consists of a sample cell, reference cell, valves, tubing, pressure transducers and temperature sensors (Fig. 2). There are two identical setups allowing two parallel measurements to be performed at the same time. The gas is injected into the setup by the MAXIMATOR DLE 5-30-GG high pressure pump and prior to the start of the experiment the system is evacuated with the use of the vacuum pump. Pressure is monitored with the use of WIKA P-30 pressure transducers of 0.05% F.S. accuracy. Pressure transducers are connected to the data acquisition system recording pressure readings every 30 second using WIKA EasyCom 2011 software.

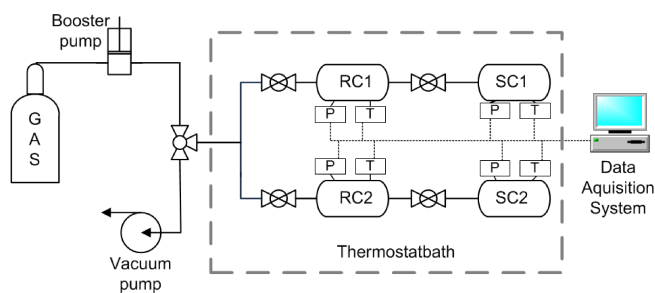


Fig. 2. Scheme of the high-pressure manometric setup

The temperature is monitored with Pt100 sensors of 1/3B class resistance tolerance. Temperature sensors are connected to the multi-channel temperature data-logger APAR AR205 which communicates with the data acquisition system.

Sample cells designed and constructed at the Silesian University of Technology are made from 304L stainless steel. The volume of the cells is 183.7 cm³ and 184.5 cm³. Sample

cells are joined to the rest of the circuit with a 1/4" NPT ISO thread. Reference cells have a volume of 151.3 cm³ and 152.5 cm³. Fittings and valves used in the setup are high pressure SWAGELOK fittings made of stainless steel with 1/4" tubing. Setup is immersed in demineralized water in custom made thermo bath with electronic temperature stabilization of 0.1°C manufactured by LABO-PLAY.

4. Results and discussion

The isotherms of CO₂ excess sorption on granulated activated carbons at 318 K were plotted versus pressure and CO₂ free phase density in Figs. 3 and 4, respectively. In all the cases a maximum sorption is observed at approximately 6 MPa of pressure. Subsequently, the sorption decreases up to 10 MPa where it slightly decreases. As it was expected, the highest sorption capacity has Filtrasorb 400 after pretreatment (samples Filtrasorb-1 and Filtrasorb-2). Although the properties seem almost identical for both the activated carbons (see Table 1), WAZ-1 has slightly lower adsorption capacity even though it was prepared in the same way as Filtrasorb 400. The maximum sorption of improperly prepared sample i.e. WAZ-2 is almost 15% lower than the same sample after treatment (drying).

In Fig. 4 where isotherms are plotted versus density an almost linear drop after the peak sorption i.e. the density of free phase 3.7–3.75 × 10³ mol/dm³ is observed. The linearity is the result of the free phase density increase approaching the density of the adsorbed phase. Extending the pressure of the experiment up to the point when the pores are fully saturated would give the adsorbed phase density value. In this case the excess sorption would be zero. In order to calculate

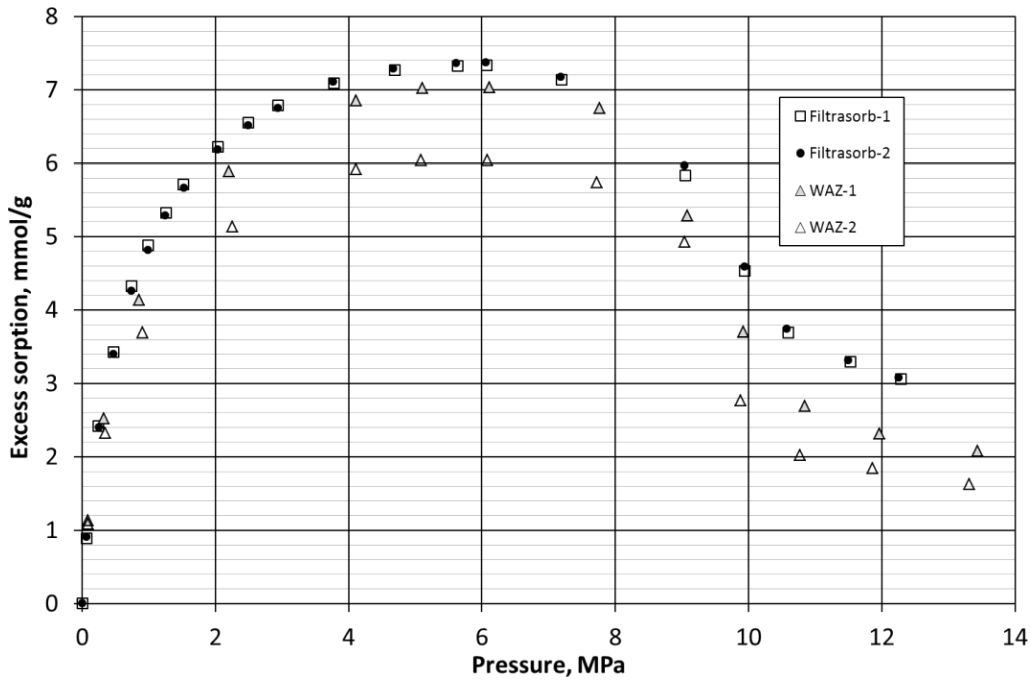


Fig. 3. Excess CO₂ sorption isotherms on granulated activated carbons at 318K plotted versus pressure

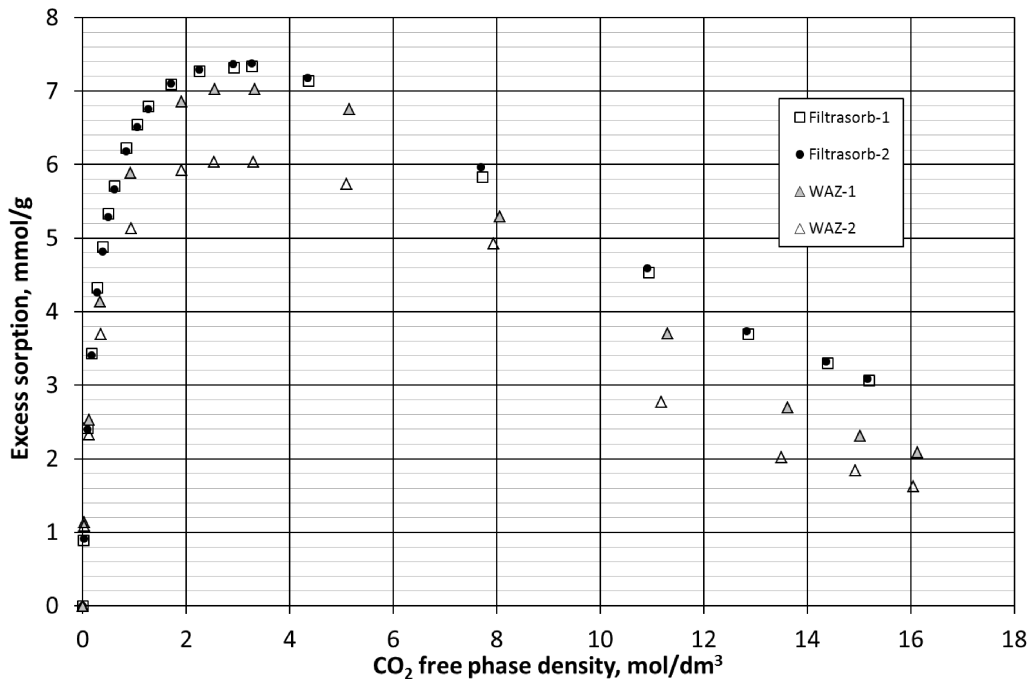


Fig. 4. Excess CO₂ sorption isotherms on granulated activated carbons at 318K plotted versus pressure

adsorbed phase density it was decided to fit a three parameter Langmuir model [28]:

$$m_{exc} = \frac{m_a \cdot \rho_g}{b_v + \rho_g} \left(1 - \frac{\rho_g}{\rho_a} \right), \quad (4)$$

where m_{exc} is the excess sorption, m_a is the maximum monolayer capacity, b_v is the Langmuir equilibrium constant (the inverse of Langmuir pressure), ρ_g is the free phase gas densi-

ty and ρ_a is the adsorbed phase gas density. Usually, the adsorbed phase density for CO₂ is assumed as the liquid phase density but for the purpose of the study it was decided to use it as a free parameter and calculate similarly to the work of [21]. Therefore, three parameters i.e. m_a , b_v and ρ_a were adjusted by minimizing residual sum of squares to the experimental data. Fitted models are added to the experimental data points as shown in Fig. 5.

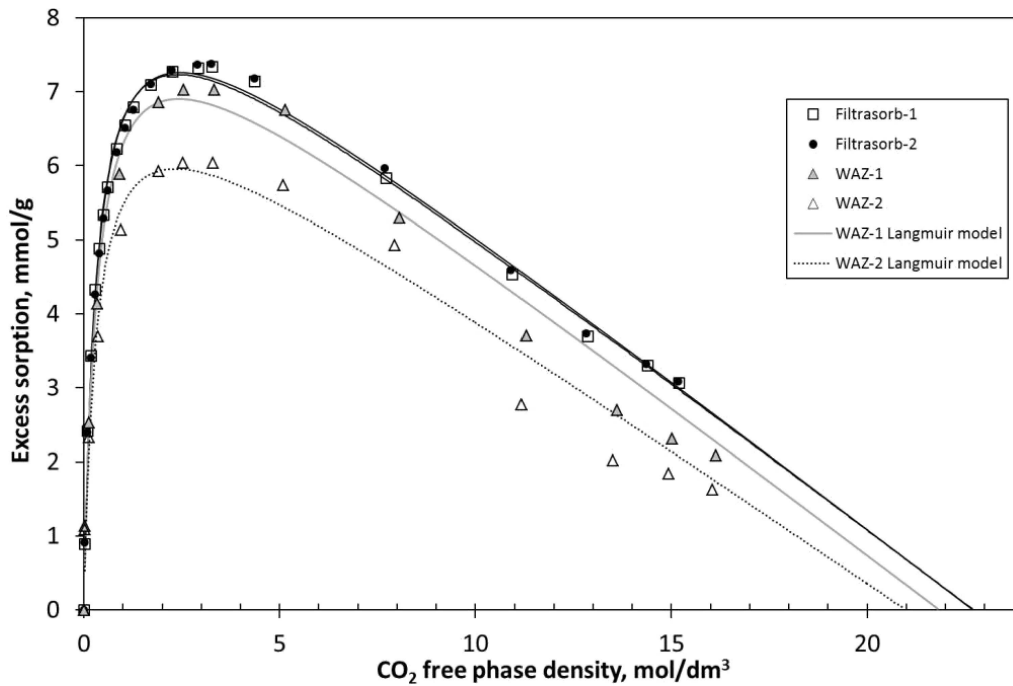


Fig. 5. Excess CO₂ sorption isotherms on granulated activated carbons at 318K plotted versus pressure with fitted three parameter Langmuir model. Solid lines are best fit model for Filtrasorb 400 samples

Calculated parameters of the Langmuir model are presented in Table 2. The shape of isotherms for Filtrasorb 400 and WAZ is similar although the lower maximum sorption capacity is reflected in the parameter m_a i.e. the maximum monolayer capacity which is lower in case of WAZ. Similar values of the b_v parameter mean that the sorption curve in the lower pressure region has the same shape. The maximum sorption capacity is almost 16% lower in sample WAZ-2 comparing to sample WAZ-1. Thus, the method of sample preparation has a great impact on the sorption capacity of activated carbon. Improperly sealed bag may result in long-term oxygen uptake from the atmosphere resulting in occupation of sorption sites. The tendency of carbon to chemisorb oxygen is greater than the tendency to adsorb any other species. Oxygen chemisorbs on the surface of GAC to form carbon-oxygen functional groups that may be acidic, neutral, or basic. This phenomena has been observed in other studies [29, 30]. Drying the activated carbon desorbs any physically adsorbed compounds from the surface and increases the capacity.

Table 2

Langmuir parameters adjusted by minimizing residual sum of squares from Eq. (4) to the excess sorption experimental data, where m_a is the maximum monolayer capacity, b_v is the Langmuir equilibrium constant, ρ_a is the adsorbed phase gas density and R^2 is the coefficient of determination

	Filtrasorb-1	Filtrasorb-2	WAZ-1	WAZ-2
m_a , mol/kg	9.17	9.26	8.87	7.66
b_v , MPa ⁻¹	0.32	0.34	0.34	0.33
ρ_a , mol/dm ³	22.71	22.70	21.8	21.0
R^2	0.993	0.992	0.977	0.952

Difference in sorption capacity of two activated carbons with the same properties i.e. Filtrasorb 400 and WAZ is difficult to explain as the bulk density (the only parameter which

is different) is not having the impact on sorption as it is calculated per unit weight. The reason for lower sorption of WAZ could be higher ash content thus lower content of organic matter where physical sorption of gases takes place.

Calculated adsorbed phase densities in case of Filtrasorb 400 are almost identical to those reported in literature [6]. Values of adsorbed densities obtained for WAZ-2 are slightly lower. Calculated sorption density of WAZ-1 is below the minimum values reported in literature [6, 21, 31, 32]. This may lead to a conclusion that “contaminated” adsorbate may decrease adsorbed phase density and lead to an erroneous measurement.

The total amount of gas residing in pores per unit mass of coal which takes into account both the adsorbed and free phase can be drawn as the absolute adsorption isotherm. In contrary to the excess sorption isotherm it represents the cumulative amount of gas adsorbed. At low pressures the excess and absolute isotherm has almost identical shape however at higher pressures the shape is affected by the density of the adsorbed phase. The most common formula applied for plotting the absolute adsorption isotherm is the transform of the following equation:

$$m_{exc} = m_{abs} \left(1 - \frac{\rho_g}{\rho_a} \right), \quad (5)$$

where m_{abs} is the absolute adsorption and the adsorbed phase density ρ_a is the value calculated with the use of a formula (4), see Table 2. Absolute isotherms were plotted versus pressure and fitted with Langmuir model in Fig. 6. The Langmuir model equation was the same as Eq. (4) with the exception of the bracketed part. Adjustment of parameters was done by minimizing residual sum of squares to the calculated absolute sorption values.

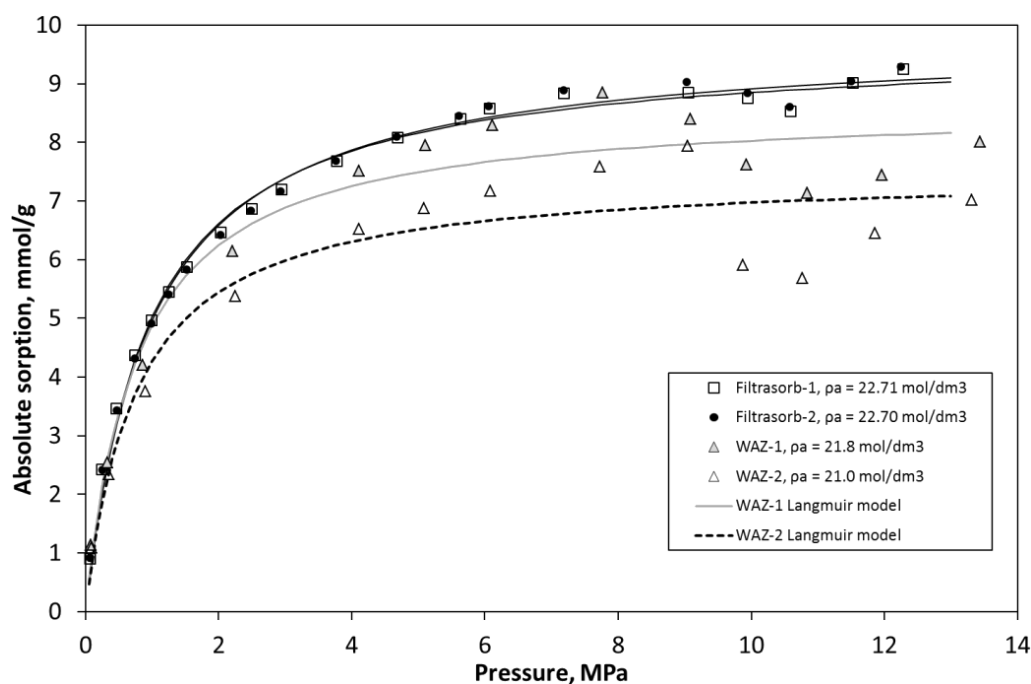


Fig. 6. Absolute sorption of activated carbons versus pressure with fitted Langmuir models at 318K. Solid lines represent Langmuir models for the samples Filtrasorb-1 and Filtrasorb-2

Despite the fact that the properties of the activated carbons used for the study are almost the same, their absolute adsorption differs significantly. Similarly to the excess sorption the highest adsorption is observed in case of Filtrasorb 400 whereas WAZ has lower sorption capacity. In the supercritical region i.e. above 8 MPa all the isotherms have visible disturbances which may be explained by experimental artifact. In case of absolute sorption the maximum sorption capacity m_a calculated by the Langmuir model for sample WAZ-2 is over 15% lower in comparison to WAZ-1. This leads to a conclusion that improperly prepared activated sample may have a higher impact on the inaccuracy measurement than a measuring error of inaccurate setup which according to [33] is lower than 10%.

5. Conclusions

In recent years CO₂ sorption on activated carbon has been a focus of many research. Despite the fact that the accuracy of sorption setups is increasing as the sorption is measured at high pressures and supercritical state, activated carbon pretreatment procedures have not been standardized while they have an impact on the obtained isotherm. Two activated carbon used for the study (Filtrasorb 400 and WAZ 0.6–2.4 mm) although with almost identical properties exhibit differences in sorption capacity. In particular, the WAZ sample which has never been in use but was not subjected to any pretreatment procedure had over 15% lower sorption than the same activated carbon dried at 373K. Three parameter Langmuir model fitted to experimental results showed different values of adsorbed phase densities for each of the activated carbons. In case of untreated WAZ sample the adsorbed phase density was lower (21.0 mol/dm³) that what is usually reported in

literature. Thus, more detailed research should be conducted in order to standardize methods of activated carbon treatment.

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REFERENCES

- [1] A.L. Goodman, A. Busch, G.J. Duffy, J.E. Fitzgerald, K.A.M. Gasem, Y. Gensterblum, B.M. Krooss, J. Levy, E. Ozdemir, and Z. Pan, "An inter-laboratory comparison of CO₂ isotherms measured on Argonne premium coal samples," *Energy Fuels* 18 (4), 1175–1182 (2004).
- [2] A.L. Goodman, A. Busch, R.M. Bustin, L. Chikatamarla, S. Day, G.J. Duffy, J.E. Fitzgerald, K.A.M. Gasem, Y. Gensterblum, and C. Hartman, "Inter-laboratory comparison II: CO₂ isotherms measured on moisture-equilibrated Argonne premium coals at 55°C and up to 15 MPa", *Int. J. Coal Geol.* 72 (3), 153–164 (2007).
- [3] Y. Gensterblum, P. van Hemert, P. Billefont, E. Battistutta, A. Busch, B.M. Krooss, G. De Weireld, and K.-H.A.A. Wolf, "European inter-laboratory comparison of high pressure CO₂ sorption isotherms II: Natural coals", *Int. J. Coal Geol.* 84 (2), 115–124 (2010).
- [4] G. Ceglarska-Stefańska and K. Zarębska, "Sorption of carbon dioxide-methane mixtures", *Int. J. Coal Geol.* 62 (4), 211–222 (2005).
- [5] A. Nodzeński and S. Holda, "Isothermic heats of methane sorption on hard coals of different ranks at elevated pressures", *Arch. Min. Sci.* 46 (4), 481–490 (2001).
- [6] Y. Gensterblum, P. van Hemert, P. Billefont, A. Busch, D. Charrière, D. Li, B.M. Krooss, G. de Weireld, D. Prinz, and K.-H.A.A. Wolf, "European inter-laboratory comparison of high pressure CO₂ sorption isotherms. I: Activated carbon", *Carbon* 47 (13), 2958–2969 (2009).

- [7] M.A. Lutynski, E. Battistutta, H. Bruining, and K.-H.A.A. Wolf, "Discrepancies in the assessment of CO₂ storage capacity and methane recovery from coal with selected equations of state Part I. Experimental isotherm calculation", *Physicochem. Probl. Miner. Process.* 47, 159–168 (2011).
- [8] S.M. Manocha, "Porous carbons", *Sadhana* 28 (1–2) 335–348 (2003).
- [9] Y. Sun, Y. Wang, Y. Zhang, Y. Zhou, and L. Zhou, "CO₂ sorption in activated carbon in the presence of water", *Chem. Phys. Lett.* 437 (1–3), 14–16 (2007).
- [10] M.C.M. Alvim-Ferraz and T.-B. Gaspar, "Impregnated active carbons to control atmospheric emissions: I. Influence of the impregnated species on the porous structure", *J. Colloid Interface Sci.* 259 (1), 133–138 (2003).
- [11] F. Stoeckli, T.A. Centeno, A.B. Fuertes, and J. Muñiz, "Porous structure of polyarylamide-based activated carbon fibres", *Carbon* 34 (10), 1201–1206 (1996).
- [12] M.C. Blanco López, A. Martínez-Alonso, and J.M.D. Tascón, "Microporous texture of activated carbon fibres prepared from Nomex aramid fibres", *Microporous Mesoporous Mater.* 34 (2), 171–179 (2000).
- [13] C.L. Mangun, K.R. Benak, J. Economy, and K.L. Foster, "Surface chemistry, pore sizes and adsorption properties of activated carbon fibers and precursors treated with ammonia", *Carbon* 39 (12), 1809–1820 (2001).
- [14] J. Przepiorski, M. Skrodzewicz, and A.W. Morawski, "High temperature ammonia treatment of activated carbon for enhancement of CO₂ adsorption", *Appl. Surf. Sci.* 225 (1), 235–242 (2004).
- [15] A. Somy, M.R. Mehrnia, H.D. Amrei, A. Ghanizadeh, and M. Safari, "Adsorption of carbon dioxide using impregnated activated carbon promoted by Zinc", *Int. J. Greenh. Gas Control* 3 (3), 249–254 (2009).
- [16] F. Dreisbach, R. Staudt, and J.U. Keller, "High pressure adsorption data of methane, nitrogen, carbon dioxide and their binary and ternary mixtures on activated carbon", *Adsorption* 5 (3), 215–227 (1999).
- [17] J. Milewska-Duda, J. Duda, A. Nodzeński, and J. Lakatos, "Absorption and adsorption of methane and carbon dioxide in hard coal and active carbon", *Langmuir* 16 (12), 5458–5466 (2000).
- [18] R. Humayun and D.L. Tomasko, "High-resolution adsorption isotherms of supercritical carbon dioxide on activated carbon", *AIChE J.* 46 (10), 2065–2075 (2000).
- [19] Y. Wang, Y. Zhou, C. Liu, and L. Zhou, "Comparative studies of CO₂ and CH₄ sorption on activated carbon in presence of water", *Colloids Surfaces Physicochem. Eng. Asp.* 322 (1–3), 14–18 (2008).
- [20] S. Himeno, T. Komatsu, and S. Fujita, "High-pressure adsorption equilibria of methane and carbon dioxide on several activated carbons", *J. Chem. Eng. Data* 50 (2), 369–376 (2005).
- [21] M. Sudibandriyo, Z. Pan, J.E. Fitzgerald, R.L. Robinson, and K.A. Gasem, "Adsorption of methane, nitrogen, carbon dioxide, and their binary mixtures on dry activated carbon at 318.2 K and pressures up to 13.6 MPa", *Langmuir* 19 (13), 5323–5331 (2003).
- [22] ELBAR "WAZ 0.6-2.4.", Katowice, 2013.
- [23] Calgon Carbon, "Filtrisorb 400" (2012).
- [24] T.L. Dantas, S.M. Amorim, F.M.T. Luna, I.J. Silva Jr, D.C. de Azevedo, A.E. Rodrigues, and R.F. Moreira, "Adsorption of carbon dioxide onto activated carbon and nitrogen-enriched activated carbon: surface changes, equilibrium, and modeling of fixed-bed adsorption", *Sep. Sci. Technol.* 45 (1), 73–84 (2009).
- [25] B.M. Krooss, F. Van Bergen, Y. Gensterblum, N. Siemons, H.J.M. Pagnier, and P. David, "High-pressure methane and carbon dioxide adsorption on dry and moisture-equilibrated Pennsylvanian coals", *Int. J. Coal Geol.* 51 (2), 69–92 (2002).
- [26] R. McCarty and V. Arp, "A new wide range equation of state for helium", *Adv. Cryog. Eng.* 35, 1465–1475 (1990).
- [27] R. Span and W. Wagner, "A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa", *J. Phys. Chem. Ref. Data* 25, 1509–1596 (1996).
- [28] R. Sakurovs, S. Day, S. Weir, and G. Duffy, "Application of a modified Dubinin-Radushkevich equation to adsorption of gases by coals under supercritical conditions", *Energy Fuels* 21 (2), 992–997 (2007).
- [29] C.H. Tessmer, R.D. Vidic, and L.J. Uranowski, "Impact of oxygen-containing surface functional groups on activated carbon adsorption of phenols", *Environ. Sci. Technol.* 31 (7), 1872–1878 (1997).
- [30] A. Dabrowski, P. Podkościelny, Z. Hubicki, and M. Barczak, "Adsorption of phenolic compounds by activated carbon – a critical review", *Chemosphere* 58 (80), 1049–1070 (2005).
- [31] E. Battistutta, P. Van Hemert, M. Lutynski, H. Bruining, and K.-H.A.A. Wolf, "Swelling and sorption experiments on methane, nitrogen and carbon dioxide on dry Selar Cornish coal", *Int. J. Coal Geol.* 84 (1), 39–48 (2010).
- [32] J. Schell, N. Casas, R. Pini, and M. Mazzotti, "Pure and binary adsorption of CO₂, H₂, and N₂ on activated carbon", *Adsorption* 18 (1), 49–65 (2012).
- [33] P. van Hemert, H. Bruining, E.S.J. Rudolph, K.-H.A.A. Wolf, and J.G. Maas, "Improved manometric setup for the accurate determination of supercritical carbon dioxide sorption", *Rev. Sci. Instrum.* 80 (3), 035103–035103 (2009).