Review article

Measurement and interpretation of supercritical CO_2 sorption on various coals

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Abstract

While the amount of CO_2 sorption data on various natural coals has increased in recent years, only few measurements have been reported under the experimental condition of supercritical CO_2 ($scCO_2$) at very high pressure (>5 MPa). The estimation of realistic CO_2-sorption capacities for different coals is crucial for the understanding of the processes associated with CO_2 storage and enhanced coalbed methane (ECBM) production.

In this study CO_2-sorption experiments up to 20 MPa at 45 °C have been performed on dry and water-containing coals from various coal basins. The coal samples cover a broad spectrum in rank, ranging from 0.52 to 2.41% vitrinite reflectance (VRr). As shown in various studies on activated carbon, $scCO_2$ surface excess sorption isotherms do not increase continuously with pressure up to complete surface coverage of the sample. This is mainly caused by the static interpretation of excess sorption isotherms, not taking into consideration changes in the sample volume such as the volume of the sorbed phase, coal swelling, etc. This leads to difficulties in the interpretation of the experimental data in terms of adsorption isotherms, as they require models for all volumetric effects. In this context, this study provides an approach to account for the volumetric effects and, hence for the estimation of total sorption capacities. For the fitting procedure, one generalized correction factor for the volume increase was calculated for each coal sample and applied to the whole experimental pressure range. Generally, it was observed that coals containing water show a smaller volume increase than their corresponding dry samples and no specific trend with coal rank was observed. Contrary, a trend for the dry samples was observed: The sample volume increase follows a U-shaped trend, i.e., decreasing from 0.5 to 1.1% VRr and increasing again from 1.1 to 1.7% VRr.
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Contents

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1. Introduction

The storage of anthropogenic carbon dioxide (CO_2) in abandoned coal mines or unminable coal seams in combination with enhanced coal bed methane (ECBM) has become a topic of increasing interest in recent years. Under European conditions several national and international projects (e.g. ICBM, RECOPOL, GESTCO, GEOTECHNOLOGIEN) are presently studying this topic or have already been completed (Wolf et al., 2002; Piessens and Dusar, 2002; Pagnier et al., 2003; Kühn et al., 2005; Busch et al., 2004, 2006; Siemons et al., 2006; Mazumder et al., 2006). The target coal seams for CO_2 injection in Europe are usually at great depth, with correspondingly high reservoir pressures and temperatures (35–50 °C, 6–15 MPa). In order to estimate CO_2-storage capacities under the P/T conditions prevailing in the target seams, accurate laboratory experiments are crucial. However, sorption isotherms measured at these high pressures and temperatures are rare in the literature. This study provides a comparison between CO_2-sorption isotherms measured on various coals that were used in the above-mentioned national and international projects.

The aim of this study is to assess the total CO_2 equilibrium sorption capacity of natural coal samples as a function of pressure with a special focus on scCO_2 conditions.

Much work has been carried out on the sorption capacity of coal with respect to CO_2 below the critical pressure (Stevenson et al., 1991; Arri et al., 1992; Yee et al., 1993; Hall et al., 1994; Nodzenski, 1998; Clarkson and Bustin, 1999, 2000; Busch et al., 2003; Goodman et al., 2004; Ozdemir et al., 2004). However, only few data have been published for higher pressures. Krooss et al. (2002) and Fitzgerald et al. (2005) performed CO_2-sorption experiments on coals between 40 and 80 °C and pressures up to 20 MPa. The results of these papers show that at high pressures (>7 MPa) the CO_2 excess (Gibbs) sorption capacity decreases with increasing pressure. A similar behavior has been observed for CO_2-sorption experiments on activated carbon at different temperatures (e.g. Humayun and Tomasko, 2000; Herbst et al., 2002).

The two commonly used methods to measure gas sorption isotherms are (1) the volumetric method and (2) the gravimetric method. The gravimetric method (e.g. Humayun and Tomasko, 2000) determines the sorption by monitoring the weight of the sample in a gas phase under well-defined P/T conditions, corrected for buoyancy effects. For the present study, the volumetric method (e.g. Mavor et al., 1990) in which sorption is determined from the pressure-change during gas transfer between a calibrated reference volume and a measuring cell was used.

At low pressures, the gas phase has a substantially lower specific density than the adsorbed phase and the volume of the latter can be neglected. In this case, the evaluation scheme results in the so called "excess sorption" or Gibbs sorption.

In high-pressure sorption experiments this is no longer the case. The measurements are affected by the non-ideality of the gas phase and volumetric effects of the condensed phases (coal swelling, increase of sorbed phase volume, etc.). The corresponding evaluation requires information or estimation on the density of the sorbed phase and the evaluation results in the "absolute

Table 1
Coal properties

Sample name	Lab.	Origin	Grain size [mm]	VRr [%]	Rank	Vitrinite [%]	Intertinite [%]	Liptinite [%]	Ash [%]	Moisture (a.r.) [wt.%]	Moisture (moist) [wt.%]
Tupton	TUD	GB	0.06–0.18	0.53	hvb C	67.2	22.8	9.2	3.0	13.5	n.a.
Silesia	RWTH	POL	<0.2	0.68	hvb B	70.0	24.0	7.0	20.1	n.a.	n.a.
Warndt I	RWTH	GER	<0.2	0.78	hvb A	79.4	10.3	10.3	3.2	0.78	1.72
Warndt II	TUD	GER	0.06–0.18	0.71	hvb A	74.4	15.6	9	4.0	n.a.	n.a.
Brzeszcze	RWTH	POL	<0.2	0.88	hvb A	15.0	71.0	14.0	19.4	n.a.	n.a.
German Creek	RWTH	AUS	<0.2	1.41	mvb	78.6	21.4	<0.1	22.1	n.a.	n.a.
Pocahontas	RWTH	USA	<0.15	1.68	lvb	89	10	1	4.74	n.a.	n.a.
Selar Cornish	TUD	GB	0.06–0.18	2.41	Semi anth.	73.6	24.6	0	7.1	0.7	23.3

sorption" values. The theoretical framework of Gibbs Surface Excess Sorption and the problems associated with the assessment of absolute sorption values have been discussed by Sircar (1999) and Sudibandriyo et al. (2003).

In the present study it has been attempted to account explicitly for these volumetric effects and to estimate total sorption isotherms from excess sorption measurements.

2. Samples

Various coal samples from different basins have been used for this study (Table 1). Fresh lumps of coal were obtained from mines in Great Britain, Germany and Poland to conduct the experiments. From these lumps representative parts have been drilled parallel to the bedding, exhibiting bright and dull coal layers to represent the variety of the coal seam. Samples from Australia and the U.S. were supplied as cores and ground coal.

The reflectance of the coals studied ranges from 0.53 to 2.41% random vitrinite reflectance (VRr) with vitrinite contents varying mostly between 67 and 89%. Only one coal (Brzeszcze) exhibits a much lower vitrinite content of only 15%. Ash contents also show a broad variety in percentages, from 3.0 to 20.1%.

3. Experimental

3.1. Sample preparation

Sorption experiments in this study were performed on different grain sizes. For some samples one specific grain size fraction was used while for others the bulk sample was crushed down to <0.2 mm (Table 1). For sorption measurements on dry coal, the powdered samples were dried under vacuum for at least 1.5 h at a temperature of 105 °C.

Moisture equilibration was carried out according to the standard ASTM D 1412-93 procedure. In the following these samples will be denoted as "moist". After moisturizing, the sample material was immediately transferred to the sorption cell. An aliquot was used for the determination of the moisture content (for further details, see Krooss et al., 2002). The wet Selar Cornish sample was prepared by immersing the coal particles in distilled water under vacuum for 3 h. Subsequently, the excess water was vacuum-filtered and the sample was transferred to the sample cell.

3.2. Experimental set-up and procedure

In this study the volumetric method was used to determine the sorption capacities of different coals as a function of pressure. The various measurements were performed in two laboratories (RWTH Aachen University and Delft University of Technology TUD) with similar volumetric set-ups which differed mainly in the volumes of the reference cell (1.16 cm^3 and 1.48 cm^3, respectively) and sample cell (9.22 cm^3 and 17.92 cm^3, respectively).

Fig. 1 shows schematically the experimental set-up, consisting of a stainless-steel sample cell, a set of actuator-driven valves, and a high-precision pressure transducer (max. pressure 18 and 25 MPa for TUD and RWTH, respectively), with a precision of 0.05% of the full-scale value. The volume between valve 1 and valve 2, including the void volume of the pressure transducer, is used as reference volume and determined by helium (He) pycnometry in a calibration run. The volumes are denoted as follows:

Reference volume: V_{ref}
Sample cell volume: $V_{\text{sample cell}} = V_{\text{sample}} + V_{\text{void}}$
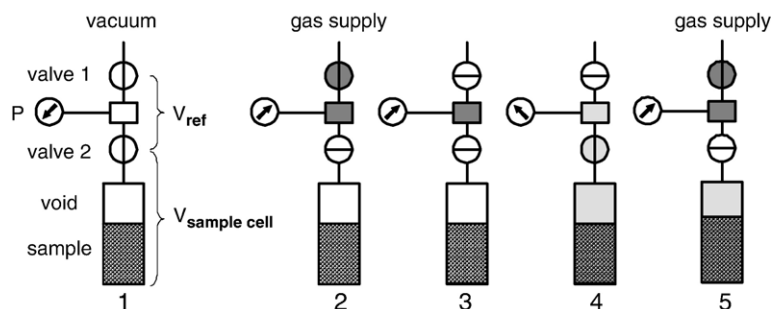
$$(1)$$

Fig. 1. Schematic flow diagram for the volumetric method for gas sorption measurements: (1) evacuation of the whole system (2) filling of the reference cell and closure of valve 1 (3) thermal equilibration, (4) valve 2 is opened, gas transfer into the sample cell, start of the sorption process (5) after pressure equilibration, valve 2 is closed and the whole procedure is started again. Steps 3 to 5 are repeated until the maximum system pressure is reached.

Taking explicitly into account the volume of the sorbed phase, one can write:

$$V_{sample\ cell} = V_{sample} + V_{void} + V_{sorbed\ phase} \qquad (2)$$

The coal samples are kept in a stainless-steel sample cell. A 2-μm in-line filter is used to prevent coal or mineral particles from entering the valves.

Each of the experimental devices is placed in a temperature-controlled oven to ensure constant temperature (± 0.2 °C) throughout the experiments. Single-gas sorption experiments were performed at 45 °C (318.15 K). At this temperature CO_2 is either in the gaseous or, at pressures above P_c, in the supercritical state. ($T_c = 304.1$ K; $P_c = 7.38$ MPa). For CO_2 measurements, maximum equilibration pressures of ~ 16 MPa and ~ 20 MPa at TUD and RWTH Aachen, respectively, were achieved.

3.2.1. Conduction of sorption experiments

Before the start of a sorption experiment, the void volume of the sample cell (V_{void}), i.e. the volume not occupied by the sorbent, is determined volumetrically using He as a non-adsorbing gas. With the known volume V_{ref} of the measuring cell, the measurement yields the void volume of the sample cell and the volume of the sample at the beginning of an experiment.

Volumetric gas sorption experiments are conducted in the sequence shown in Fig. 1. At the beginning of the experiment both the sample cell and the reference cell are evacuated to establish a defined starting condition (step 1). Subsequently, the two cells are separated by closing the shut-off valve 2.

In the next step, a certain amount of gas is admitted to the reference volume by opening the gas access valve 1 (step 2). After closing this valve, 45–60 min are allowed

for pressure and thermal equilibration (step 3). During this period, the pressure in the reference cell is monitored. The shut-off valve 2 between the cells is then opened and the sorbate gas is admitted to the sample cell (step 4). Sorption starts and gas molecules are removed from the free gas phase, resulting in a pressure drop in the free gas phase. This pressure drop is accurately monitored at time intervals between 1 s and 30 min until pressure equilibrium is achieved. Depending on coal type, particle size and pressure, between 1 h and up to 20 h are required to establish sorption equilibrium. After recording the equilibrium system pressure, the cells are separated again (step 5). These steps are repeated until the maximum pressure level of the individual set-up is reached.

The equation of state (EOS) for CO_2 developed by Span and Wagner (1996) was used throughout this work. The equation is considered to be the most reliable EOS and is based on the latest and most comprehensive sets of experimental data. The EOS was used to compute the amount of substance (moles of gas) in reference and sample cell from the gas pressure, temperature, and the volumes of the cells.

Helium densities were calculated by a van der Waals equation of state with "a" and "b" parameter values reported by Michels and Wouters (1941).

3.2.2. Isotherm models

The Langmuir model is a simple sorption model and widely used for the assessment of high-pressure gas sorption on coal in particular and on microporous media in general. It is also used to describe the dissolution (absorption) of gases in e.g. clathrates (Van der Waals and Platteeuw, 1959; Zhu et al., 2005). This model is commonly used to represent supercritical CO_2-sorption data on coal (e.g. Ozdemir et al., 2003; Sudibandriyo et al., 2003; Fitzgerald et al., 2005). The applicability of different adsorption models for gas adsorption on coal is

described by Clarkson et al., 1997. The Langmuir sorption isotherm is given as:

$$n_L^{sorb} = \frac{n_L P}{P + P_L},\tag{3}$$

with n_L^{sorb} denoting the sorbed mass, P the gas pressure, P_L and n_L the Langmuir parameters for Langmuir pressure and molar mass, respectively.

For comparison, the Dubinin–Astakhov (D–A) model (Dubinin and Astakhov, 1971) was chosen to represent the sorption isotherm for Silesia coal. The D–A model is given as follows:

$$w = w_0 \exp\left(\left[\frac{RT}{\beta E}\ln\frac{P_s}{P}\right]^n\right),\tag{4}$$

where w represents the volume of the adsorbate, w_0 the micropore volume, R the universal gas constant, T the temperature, β the sorbate affinity coefficient, E the characteristic energy, P_s the pseudo saturation vapor pressure, P the experimental pressure and n the heterogeneity factor. Parameters in this model are βE, P_s, and n. Here, P_s is estimated using the empirical formula proposed by Dubinin (1975) for any temperature beyond T_c. The adsorbed amount is determined by:

$$n^{sorb} = w_0 \exp(-(A/E)^n),\tag{5}$$

where A is defined as the differential molar work of adsorption (Dubinin and Astakhov, 1971).

4. Experimental results

Excess (Gibbs) sorption isotherms have been determined for CO_2 on moist, "as received", and dry coal samples at 45 °C. Fig. 2 shows the result of these experiments for the different coal samples on a dry, ash-free basis. As expected, sorption capacities for dry samples are higher than for coals containing water with maximum values of $\sim$2.2 mmol/g for the Silesia and Tupton coals (Figs. 2 and 3). For the samples investigated here, no trend is observed for sorption capacity with respect to rank for the dry samples. However, coals containing water (Table 1) show this trend and the sorption capacity increases (from 0.7 to 1 mmol/g) with increasing rank and decreasing moisture content.

Furthermore, Figs. 2 and 3 show different shapes of the isotherms for dry samples and samples with certain moisture content. The dry samples exhibit a maximum in the excess sorption isotherm between 8–10 MPa, followed by a sharp decrease. However, for the "moist" and "as received" samples a different behavior is observed. Sorption isotherms show a smooth decrease in excess sorption values above 8–10 MPa. It is interesting to note that the Brzeszcze dry, German Creek dry, and Warndt "as received" samples tend to achieve saturation in sorption capacity. Other samples do not show this behavior and rather a continuous decrease in excess sorption capacity above 8–10 MPa can be recognized.

5. Void volume correction

5.1. Uncertainties in estimating volumetric effects during CO_2 sorption

Several volumetric effects are reported in the literature and have to be taken into account. Four aspects are briefly discussed here.

One initial uncertainty is the calculation of the absolute sorption capacity, assuming a certain density of
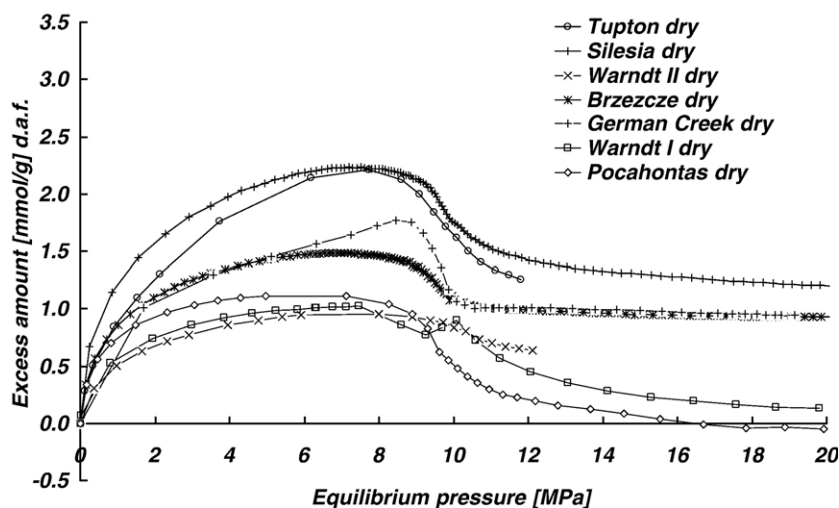

Fig. 2. Excess sorption for different dry coals samples, measured at 45 °C.
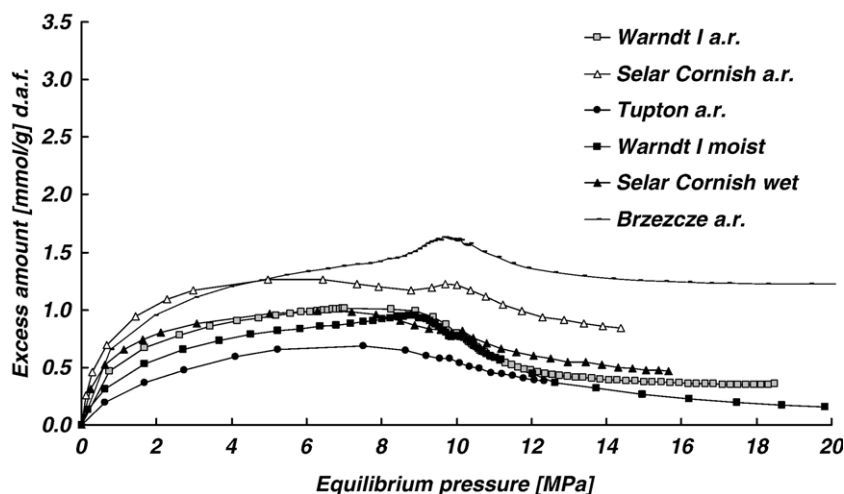
Fig. 3. Excess sorption for different coal samples containing water, measured at 45 °C.

the sorbed phase. This approach can be used for CO_2 isotherms, considering a constant density of the sorbed CO_2 phase, independent of pressure and temperature. However, sorbed phase CO_2 density values given in literature vary greatly (Table 2).

Based on the excess sorption isotherm for Silesia coal in the "as received" moisture state, the absolute sorption capacity has been computed (Fig. 4) using the sorbed gas densities in Table 2. The calculation is based on the following equation (e.g. Mavor et al., 2004):

$$n_{abs} = \frac{n_{ex}}{1 - \frac{\rho_{gas}}{\rho_{ads}}} \qquad (6)$$

where n_{abs} and n_{ex} denote the absolute and excess sorption capacities (e.g. in mmol/g), respectively, and ρ_{gas} and ρ_{ads} are the density of the free gas and the adsorbed gas phase, respectively. The resulting absolute sorption isotherms in Fig. 4 demonstrate the dependence of the absolute sorption capacity on the value assumed for the sorbed gas density. This introduces a significant uncertainty in the determination of absolute sorption values.

A second volumetric factor that needs to be considered is the ability of coals to swell when interacting with CO_2, particularly scCO_2. This topic is subject of recent research, however only few quantitative studies have been published so far. Karacan (2003) performed a detailed X-ray computed tomography study on a bituminous coal sample and found that CO_2 sorption and swelling is heterogeneous within a coal sample and depends on the different lithotypes. Laximinarayana et al. (2004), Zutshi and Harpalani (2004), Reucroft and Sethuraman (1987) and Reucroft and Patel (1986) found a

volumetric increase due to coal swelling of 0.26–4.2% at pressures varying from 0.1 to 15 MPa. Reucroft and Sethuraman (1987) found that swelling increases with increasing pressure and decreases with increasing coal rank. For the various coals the determination of swelling factors is difficult and time-consuming but crucial for the assessment of absolute CO_2 sorption isotherms. So far, the determination of absolute sorption isotherms does not consider this effect and, therefore, still bears additional and significant uncertainties in the total sorption capacity.

Further, CO_2 is able to dissolve (absorb) in the coal polymer structure as described by Larsen (2004). This effect might have additional impacts on the estimation of absolute sorption capacities; for example, Mahajan (1991) states that compared to CO_2, He is not able to dissolve into the coal polymer structure, resulting in an underestimation of the void volume accessible to CO_2.

Hol et al. (2005) and Kolak and Burruss (2006) observed chemical changes of coals with scCO_2. The latter found for coal samples of various rank that alkane

Table 2
Adsorbed phase densities of CO_2 based on literature values

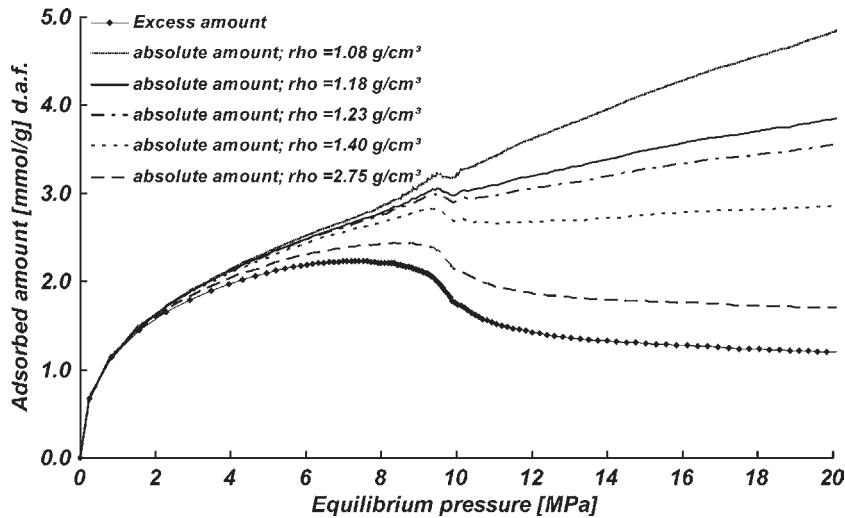| CO_2 density (g/cm^3)	Source
1.080	Hall et al. (1994)
1.178	Saturated liquid density at triple point (Span and Wagner, 1996)
1.227	Liquid density at boiling point (IUPAC, 1976)
1.40	Fitzgerald et al. (2005)
2.75	Humayun and Tomasko (2000)

Fig. 4. Calculation of absolute sorption for Silesia sample taking into account various sorbed CO_2 densities.

concentrations are mobilized, while the highest amounts were measured for lignites, the lowest for anthracites.

Another uncertainty is associated with He-pycnometry measurements to determine the solid/free gas volume. Here, He is considered to be a non-sorbing gas which, in fact, has been shown to be incorrect at low temperatures and high pressures (Malbrunot et al., 1997).

A fourth uncertainty may be introduced due to the change in the coal volume at higher pressures activated by compression or shrinkage (Ozdemir et al., 2003). This observation may have an opposing effect: the coal gets compressed at high pressures, hence decreasing the solid volume. At the same time, pore entrances may be closed due to this compression, consequently prohibiting gas molecules from entering these pores, resulting in an increase in the solid volume. However, these opposing effects are difficult to quantify and can only be incorporated in a general volume factor.

In summary, these different effects bear important uncertainty factors in the determination of total sorption isotherms and, at the present state of research, it is difficult to separate them from each other. In the further course of this study, only one factor will be determined accounting for all volumetric effects associated with CO_2 sorption on natural coals.

5.2. Void volume correction procedure

Following the procedure of Mavor et al. (1990), the amount of sorbed gas (n^{sorb}) is defined as the difference between the total amount of gas n^{tot} present in the system and the amount of gas (n^{gas}) occupied by the

void volume (V_{void}). The amount n^{gas} is calculated from the molar concentration (c^{gas}) in the free gas phase obtained from the equation of state. Hence we obtain:

$$n^{sorb} = n^{tot} - n^{gas} := n^{tot} - c^{gas} V_{void}. \qquad (7)$$

The value for V_{void} has to be found over the entire pressure range such that sorption data points can be represented by a non-decreasing function of pressure, e.g. by the Langmuir function (Eq. (3)). Three unknown parameters, n_L and P_L describing the Langmuir isotherm, and a void volume value V_{void} have to be determined. In this interpretation, a single value of V_{void} (Eq. (7)) was chosen to keep the problem uniquely defined. The three parameters are not determined at once but with the use of a stepwise procedure as follows:

1. Determination of n^{sorb} (Eq. (7)) with the initial void volume determined by He-pycnometry (filled diamonds in Fig. 5).
2. Determination of the theoretical Langmuir sorption amount n_L^{sorb} using n_L and P_L parameters. This is done for the pressure range where the initial excess isotherm is monotonically increasing (up to ∼ 7.5 MPa), shown as a black line in Fig. 5.
3. Extrapolation of the Langmuir isotherm towards the end pressure of the individual experiment.
4. Calculation of the sum of squared differences with a target function T (Eq. (8)). The target function,

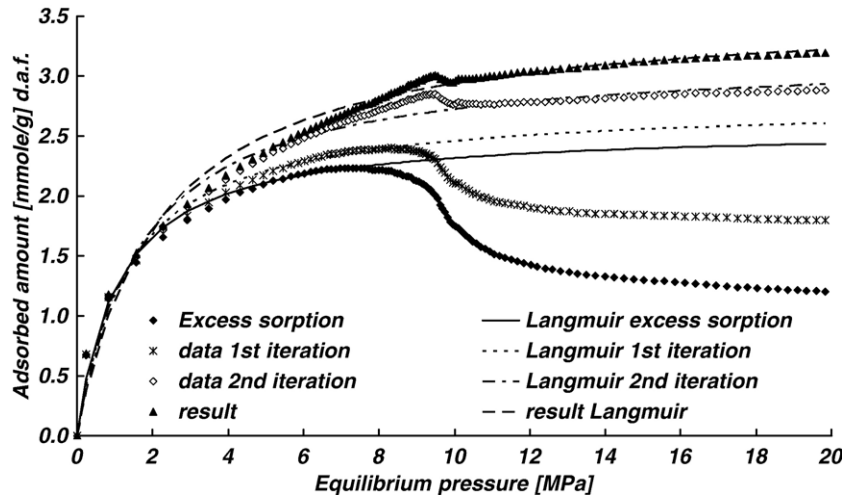$$T = \sum_i (n_i^{sorb} - n_{Li}^{sorb})^2 \qquad (8)$$

Fig. 5. Sorption isotherms of Silesia coal sample. Documented are the experimental data points (symbols) and their corresponding Langmuir isotherms (lines). In the first iteration step, the void volume was decreased by 2.1% (stars), in the second by 5.2% (open diamonds) and for the final result by 5.7% (filled triangles).

is minimised with respect to the three parameters e.g. the void volume V_{void} and the Langmuir parameters n_L and P_L.

5. The void volume is changed to find an optimal value of T (Eq. (7)).
6. The Langmuir parameters are changed to find an optimal value of T (Eq. (3)).
7. Steps 4 and 5 are repeated until no further minimisation for T can be obtained (see Fig. 5).

For the implementation of this optimisation procedure, the Excel solver function was utilised, which, in our case, used the Newton Raphson scheme with a central difference.

This resulting isotherm is called the total sorption isotherm (filled triangles in Fig. 5). It is seen that by this procedure excess sorption values are forced to follow the monotonically increasing Langmuir isotherm.

In addition to using the Langmuir formulation, the iterative scheme based on the D–A model (Eq. (4)) was applied to Silesia coal. The heterogeneity factor n is obtained by a least squares fit and its optimal value was found to be 1.65, i.e. well within the range for microporous adsorbents. The empirical Dubinin equation (Dubinin, 1975) for the pseudo saturated vapor pressure P_s yielded a value of 8.09 MPa. This means, that the sorption isotherm is not defined above this pressure
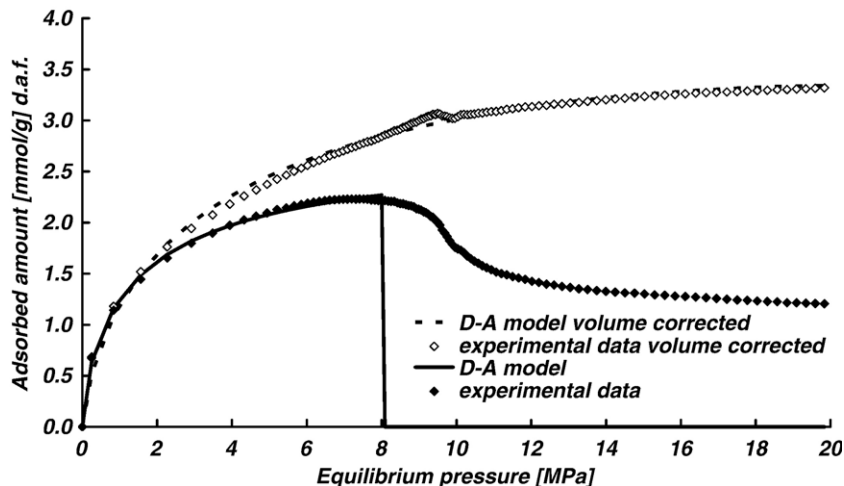

Fig. 6. Silesia dry sorption isotherm and corresponding D–A model isotherm for the original and volume corrected data. The D–A model is not defined beyond the pseudo saturation vapor pressure. The volume corrected isotherms assume a pseudo saturation vapor pressure of 20 MPa.
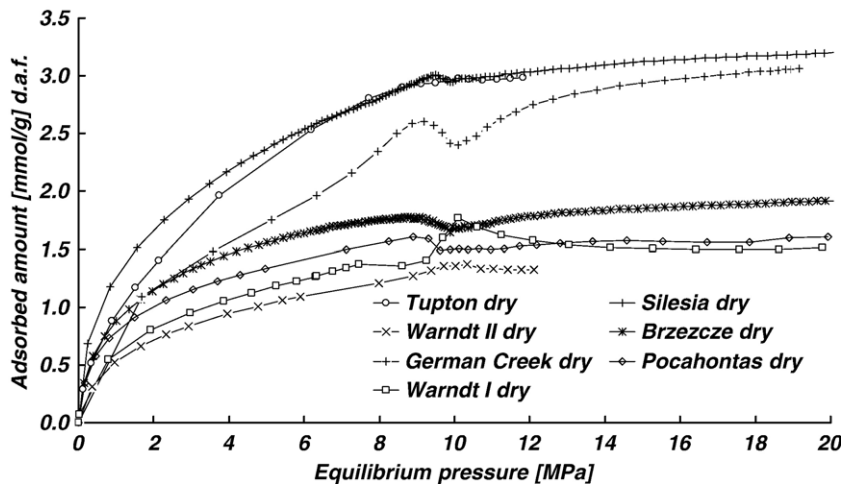
Fig. 7. Results of the void volume fitting for different dry coal samples.

value (Fig. 5). However, the P_s-value saturation vapor pressure can be chosen along with the experimental end pressure, the heterogeneity factor n, and βE to fit the experimental data over the whole pressure range. Results are shown in Fig. 6. The maximum sorbed amount at 20 MPa is with 3.32 mmol/g somewhat higher than predicted by the Langmuir model (3.20 mmol/g).

5.3. Void volume correction results

The iterative scheme for the Langmuir model was applied to all measured excess sorption isotherms (Figs. 7 and 8).

Trends observed for the excess sorption are also valid for the total sorption isotherms: coals containing water

adsorb less than dry coals and show an increasing sorption capacity with increasing rank. Langmuir volumes for total sorption capacities are 17 to 45% higher than the corresponding excess sorption capacities.

The shape of the isotherms changes significantly and can be separated in three domains. All isotherms show a monotonically increasing sorption capacity from zero to ∼8–9 MPa. From ∼9–11 MPa the isotherms show an increase followed by a decrease in sorption capacity. Beyond 11 MPa, no general trend is recognizable. Isotherms exhibiting a high sorption capacity (above 1.5 mmol/g) show a moderate rise in sorption capacity with pressure. With the exception of Warndt I ("as received"), isotherms measured on coals containing water decrease slightly. However, the steep decrease of excess sorption isotherms beyond ∼9 MPa shown in Fig. 3 has
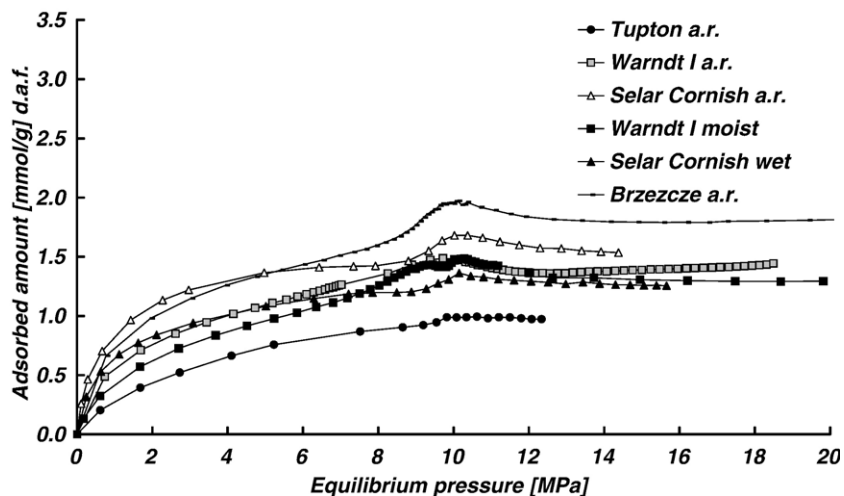

Fig. 8. Results of the void volume fitting for different coal samples containing water.

Table 3
Sample weight and Langmuir parameters of the excess and total sorption isotherms

Sample	Weight [g] d.a.f.	Excess sorption isotherms			Total sorption isotherms		
		P_L [MPa]	n_L [mmol/g]	Initial V_v (cm^3)	P_L [MPa]	n_L [mmol/g]	Changed V_v (cm^3)
Tupton dry	10.871	1.70	2.65	9.723	2.61	3.69	8.448
Tupton ar	12.306	2.34	0.91	8.266	3.77	1.31	7.787
Silesia dry	3.684	1.09	2.57	5.926	2.13	3.56	5.527
Warndt II dry	12.187	1.20	1.13	7.791	2.42	1.62	7.364
Warndt I dry	3.931	0.48	1.20	6.281	1.64	1.69	5.987
Warndt I a.r.	6.249	1.31	1.04	5.884	2.24	1.63	5.626
Warndt I moist	4.202	1.53	1.06	6.996	2.46	1.49	5.736
Brzeszcze dry	3.141	0.92	1.68	6.237	1.50	2.03	6.069
Brzeszcze a.r.	3.676	1.33	1.63	5.489	1.88	2.09	5.339
German Creek dry	3.188	2.31	2.19	7.028	5.78	4.01	6.657
Pocahontas dry	3.097	0.52	1.21	6.696	1.08	1.68	6.417
Selar Cornish a.r.	12.761	0.62	1.41	8.310	0.96	1.70	7.824
Selar Cornish wet	10.207	0.65	1.064	9.781	1.08	1.384	9.311

vanished. For isotherms with end pressure values of 20 MPa this decrease cannot be observed.

The comparison of the excess sorption and total sorption isotherms yields an overall increase in total sorption capacity for all samples after the volume correction was applied (Table 3). For the dry samples, the Langmuir volume increased between 20 and 44% with the exception of the German Creek sample (increase of ∼ 83%). For the samples containing water, this increase in Langmuir volume is smaller, ranging from 30 to 44%.

In order to quantify the volumetric effects, the increase of the coal volume was calculated from the reduction of the void volume and plotted versus rank for the different measurements (Fig. 9). Generally, there

seems to be a difference between the measurements on dry coals and coals containing water. No specific trend can be observed for the coals containing water while for the dry coals the increase in coal volume decreases at low rank and increases again at higher rank with a minimum at ∼ 1.1 to 1.3% VRr. In particular, the low rank coals show a large increase in volume (∼ 11–13%). Coals containing water show no rank dependency. The volume increase for all samples varies between 4 and 8%. The Tupton coal sample shows a ∼ 9% difference in volume increase between the dry and "as received" (13.5% H_2O) samples. For the highest rank Selar Cornish "as received" (0.7% H_2O) and wet (23% H_2O) samples, such large difference has not been observed. Here the difference is only ∼ 0.2%.
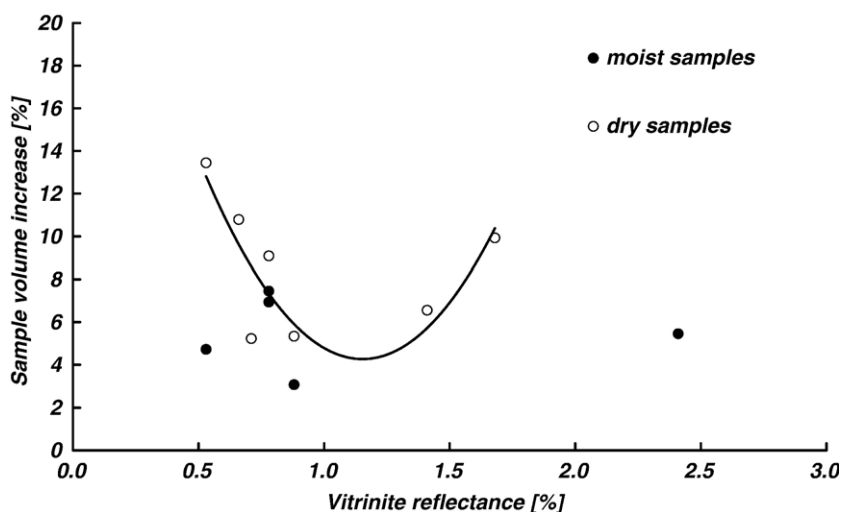

Fig. 9. Results of the calculated coal volume increase for dry and water-containing samples. The trend line indicates a fit for the coal samples in the dry state.

6. Discussion

6.1. Excess and total sorption isotherms

Two different volumetric sorption devices have been used for this study, designed in a similar way but with different volumetric dimensions. No sample has been measured in both set-ups to compare the quantitative results. The reason for this is that all coal samples were collected and measured for different projects. However, the two different Warndt coals originate from the same colliery and are very similar in coal properties (difference in vitrinite reflectance is 0.06% VRr). Both isotherms show a similar shape and similar excess sorption (1.20 and 1.13 mmol/g) and total sorption values (1.63 and 1.69 mmol/g) for the dry samples, respectively (Table 2). This justifies the comparison of quantitative results obtained with each set-up.

The coal samples used in this study originate from various coal basins. Coals from different coal basins are difficult to compare since the coal basin evolution (e.g. degree of metamorphism) and the organic precursors are different (Prinz, 2004; Ceglarska-Stefańska and Zarêbska, 2005). This leads to variations in the structure and composition of the coals of the same rank and therefore to variations in the adsorption capacity.

The comparison of the excess sorption shows no trend in sorption capacity with coal rank. Even if coal rank dependence can be observed for coals originating from the same coal basin, this trend cannot be observed for coals from different coal basins as explained above.

Only Tupton, Warndt I and Brzeszcze coals have been measured in the dry state as well as with a certain moisture content. A comparison yields a higher sorption capacity for the dry samples. This observation is a common knowledge and has already been published in literature (e.g. Levy et al., 1997; Clarkson and Bustin, 2000; Krooss et al., 2002). Nishino (2001) found that water competes with carbon dioxide for adsorption sites and therefore reduces the sorption capacity for CO_2.

6.2. Non-linearity effects in the near critical region

An unusual feature of some excess sorption isotherms is expressed in the 8 to 10 MPa region (Figs. 2 and 3) where in some instances the isotherm shows an increase followed by a decrease in sorption capacity.

This may be attributed to one or a combination of the following reasons. First, a possible inadequacy of the EOS in the near critical region may lead to inaccurate density estimates. Sun et al. (2005) compared precise PVT experiments with the CO_2 density values calculated from the Span and Wagner EOS (Span and Wagner, 1996) and found that specifically near the critical region density data may vary up to 0.1%. It is unlikely that this has a strong effect on the shape of the isotherm in the near critical region. Secondly, as described in a study by Cahn (1977) and reviewed by De Gennes (1985) a first order wetting transition takes place somewhat below the critical point. This means that the adsorbed phase near the surface shows a sudden increase in density at the so called wetting temperature $T_w < T_c$. Possibly, such effects can also occur when the pressure approaches the critical region. This idea is supported by Humayun and Tomasko (2000), who found the same phenomena when measuring CO_2 sorption on activated carbons up to 20 MPa at various temperatures (30.5–45 °C). The explanation they give is that the calculated density in this region, based on the assumption of a constant adsorbed phase volume, is greater than the liquid phase density of the CO_2.

Thirdly, the non-monotonous behavior observed can also be an artifact of the conversion of P, T, and volumes to CO_2 density. The accuracy of the temperature control was 0.1–0.2 °C. Similar inaccuracies in the temperature control have been recorded for high-pressure CO_2-sorption experiments by Fitzgerald et al. (2005) and Krooss et al. (2002). This inaccuracy may introduce an error in the estimation of CO_2 density of up to 1.2% for the experimental temperature used and, hence, may change the shape of the isotherm visibly near the critical CO_2 density.

Finally, state of the art sorption models do not consider a transition from a gaseous state to a supercritical high density state. The Langmuir model only considers the interaction between the sorbed molecule and the matrix whereas models based on the theory of micropore filling explicitly consider an interaction between the adsorbate and the adsorbent in the subcritical region (Aranovich and Donohue, 1997). In this study, the data was fitted with two different sorption models. The S-shaped part of the experimental sorption isotherm remains localized near the critical point. Therefore it is concluded that the anomalous behavior in the critical region is responsible for the observed deviations.

6.3. Volumetric effects

It is well known that volumetric effects occur during sorption measurements. These volumetric effects successively increase the sample volume and, hence reduce the void volume during the experiment. This effect becomes visible when the volume increase can no longer be compensated by gas uptake in the coal porous structure.

This leads to the "apparent" decreasing sorption behavior above ∼ 8–10 MPa.

As mentioned earlier, several volumetric effects need to be accounted for which are, however difficult to distinguish. Therefore, a single value volume correction has been applied to the whole excess sorption measurement in this study. This approach results in monotonically increasing total sorption isotherms for experiments attaining high final pressure values (20 MPa).

However, after fitting experiments with lower end pressures a slight decrease is still visible. This may be related to the fact that complete gas saturation has not been reached for these samples. Therefore, it is assumed that correcting for an increase in coal volume is difficult to perform for samples measured up to low or medium pressures where no maximum gas saturation has been achieved.

Ozdemir et al. (2003) provide a model to account for the increase in coal volume in volumetric sorption measurements, measured on Argonne Premium Coal Samples at 22 °C and pressures up to 3.5 MPa. The correction includes the swelling or shrinkage of the solid phase, the uncertainties associated with He-pycnometry and a certain volume change due to the dissolution of the sorbing gas. Ozdemir et al. (2003) applied this correction to absolute sorption isotherms where the density of the sorbed phase has already been accounted for. Values for this density, as discussed in the literature (Table 2), vary tremendously (Fig. 4). For this reason it is more appropriate to use only one factor to account for all volumetric effects, including the density of the sorbed phase. Additionally, a good fit of the $scCO_2$ excess sorption isotherms can only be achieved by determining very high-pressure sorption isotherms (above ∼ 10 MPa). Here the pressure range where coal has reached or is close to reach maximum surface coverage has been accounted for.

Assuming that volumetric effects are small at low pressures total sorption capacities calculated are over-estimated in this pressure range. This is because the same factor for the volumetric increase has been applied over the whole experimental pressure range in this study. However, the increase in total sorption is less than 5% at 1 MPa and less than 10% at 3 MPa compared to the excess sorption, indicating that the inaccuracy is rather small. At very high pressures (>15 MPa) this effect decreases because it can be assumed that the coal sample is achieving saturation and the volume increase successively diminishes.

The comparison of the excess sorption and total sorption isotherms yields an overall increase in sorption capacity for all samples (Table 3). Furthermore, no trend in sorption capacity with coal rank was observed for the samples investigated, before and after the volume correction.

6.4. Rank dependent volumetric effects

Results of the volume correction for dry coals and coals containing water are plotted in Fig. 9. For dry coals the increase in volume decreases with rank increase in the low rank range (<1.1% VRr). Similar results have been reported by Reucroft and Sethuraman (1987), who reported a decrease in coal swelling from lignite to high volatile bituminous rank. In this study, the increase in coal volume decreases (from 13 to 5%) and exhibits a minimum around 1.1–1.3% VRr. After passing this minimum, the coal volume increases again (up to 10%) for the coal samples investigated in this study. The minimum between these two trend lines coincides with the minimum in the micropore volume of dry coals with rank as reported by Prinz and Littke (2005). In different studies it is assumed that sorption mainly takes place in the microporous system of coals (e.g. Crosdale et al., 1998; Clarkson and Bustin, 1999). If the micropore volume correlates with the sorption capacity it seems to be reasonable to expect that volumetric effects are partly dependent on this relationship.

Coals containing water do not show any specific trend for the volume increase with rank. The volume increase varies between 4 and 8%, independent of rank and moisture content. However, the full rank range has not been covered by our measurements. Especially above 1% VRr, there is a lack of representative experimental data. The reason for the effect of water is, so far, not well understood. A further investigation of the influence of coal rank on the volume increase of coals containing water is required.

7. Conclusion

- Sorption measurements with $scCO_2$ on various coals have augmented the available data set in the literature.
- The data, partly measured at TU Delft and RWTH Aachen, show similar trends.
- The interpretation of the data requires a high-resolution equation of state (EOS). The Span–Wagner EOS (Span and Wagner, 1996) appears to be adequate for our purposes.
- Both, the Langmuir and D–A model have been used to estimate several volumetric effects related to CO_2 sorption on coal. With this volume correction the measured data show monotonous behavior except around the critical region.
- Small oscillations in the isotherms around the critical region are attributed to the variation in the adsorbed phase density near the critical point.
- The Langmuir mass for the total sorption isotherms is generally 20–44% higher than for the excess sorption isotherms.

- For dry coals, the volume correction factor shows agreement with micropore volume changes as a function of rank as reported by Prinz and Littke (2005).
- For wet coals, volume correction factors are generally smaller; however, no trend can be discerned in the few points measured.
- The procedure described in this paper leads to a more accurate estimate of the sorption capacity of carbon dioxide in coals. However, a fundamental model that describes sorption behavior in the supercritical region is still missing.
- In addition, the procedure quantifies rank dependent swelling effects during high-pressure sorption in coal.

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