CO₂ AND CH₄ Sorption Kinetics on Coal: Experiments and Potential Application in CBM/ECBM Modeling

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ABSTRACT

Numerical modelling of the processes of CO₂ storage in coal seams and enhanced coalbed methane (ECBM) production requires information on the kinetics (rates) of the sorption/desorption processes. In order to address this issue which is of relevance in different EU-projects (ICBM, RECOPOL, Siemons et al. 2003), the sorption kinetics of CO₂ and methane were studied on a high volatile bituminous coal (VRr = 0.68 %) from the Upper Silesian Basin, Poland, in the dry and moisture-equilibrated state. The experiments were conducted on six different grain size fractions, ranging from <63 µm to >2000 µm at temperatures of 45°C and 32°C using a volumetric experimental set-up. CO₂ sorption was consistently faster than methane sorption under all experimental conditions. Further qualitative results showed that moisture in the coal leads to a significant reduction in the sorption rates by a factor of >two and that the sorption rate is positively correlated with temperature. Generally, adsorption rates decreased with increasing grain size for all experimental conditions. Based on the experimental results simple modelling approaches are proposed for the sorption kinetics of carbon dioxide and methane that may be readily implemented into reservoir simulators. Evaluation of the fitting parameters resulted in a two phase process associated with the combined adsorption/diffusion process, one slow and one rapid process. These two processes have been compared in terms of a dependency of grain size.

INTRODUCTION

Coalbed methane (CBM) production combined with CO₂ injection is presently an issue of intense investigation worldwide. This combination is expected to be advantageous in terms of enhancing the CBM production (ECBM) and providing at the same time an opportunity for the subsurface storage of large amounts of CO₂. The effect would be a reduction of greenhouse gas emissions as required by the Kyoto agreement.

On the European level the feasibility of CO₂ storage in coal seams is presently being investigated in the EC RECOPOL project which involves laboratory tests, numerical modelling and a pilot injection into Carboniferous coal seams in the Upper Silesian Basin in Poland. It is, in this context, the first project of this kind outside North America. The laboratory tests currently performed at RWTH-Aachen provide fundamental data on the gas (CO₂ and methane) storage capacity of dry and moist coal (Krooss et al. 2002; Busch et al. 2003a) as well as information on the adsorption behaviour from mixtures of the two gases (preferential sorption, Busch et al. 2003b).

Another major aspect of CO₂ storage and the combined CO₂-enhanced CBM recovery is the rate or kinetics of CO₂ sorption and methane desorption. To address this issue we conducted sorption kinetic experiments with both CO₂ and methane on six different grain size fractions (from <63 µm to >2000 µm) of a selected coal sample from the Upper Silesian Coal Basin. The purpose of this study was (I) to define a simple empirical model describing the adsorption rates of the two gases, (II) to attempt an extrapolation of the data from the laboratory (grain-size) scale to the reservoir scale (cleat spacing).

SAMPLE

All experiments reported here were performed on one single coal sample from the Silesia mine in the Upper Silesian Basin in Poland. It is a high-volatile bituminous coal from the Upper Carboniferous (Pennsylvanian) with a vitrinite reflectance of 0.68 %. Its maceral composition is dominated by vitrinite (70%). The coal was obtained as a lump from a depth of ~900 m.
EXPERIMENTAL

Sample preparation

The crushed Silesia coal sample was divided and aliquots were sieved into six different grain size fractions: <63 µm, 0.063 - 0.177 mm, 0.177 – 0.354 mm, 0.354 – 0.707 mm, 0.707 – 2.0 mm to >2000 µm. For adsorption measurements on dry coals, the powdered samples were dried in the adsorption cell under vacuum for 1.5 hours at a temperature of 105°C. It is known that the sieving process may result in partial enrichment or depletion of coal macerals in certain grain size fractions. Cloke et al. (2002) give a very detailed overview of maceral and ash fractionation during sieving. This issue will be addressed in the conclusions. Moisture equilibration was carried out according to the “Standard Test Method for Equilibrium Moisture of Coal at 96 to 97 Percent Relative Humidity and 30°C” (ASTM D 1412 – 93). After moisturising, the sample material was transferred immediately to the adsorption cell. An aliquot was used for determination of the moisture content. For further details cf. Krooss et al. (2002).

Experimental set-up for sorption kinetic experiments

Figure 1a shows a scheme of the experimental set-up for single component gas adsorption and sorption kinetic experiments. The device consists of a stainless-steel sample cell, a set of actuator-driven valves and a high-precision pressure transducer (max. pressure 25 MPa, with a precision of 0.05 % of the full scale value). The volume between valves V2 and V3, including the dead volume of the pressure transducer, is used as reference volume (see below) and determined by helium expansion in a calibration procedure. The powdered coal samples are placed into the calibrated sample cell. An in-line filter with 2 µm pore size prevents coal or mineral particles from entering the valves. The sample cell is kept in a thermostated oven, the temperature of which is constant to ±0.1°C of the set-point. Figure 1b shows the definitions of the volumes relevant for the volumetric measuring procedure.

To monitor the rate of the sorption process pressure data points were initially taken every second and then at one minute intervals until complete equilibration of the gas phase with the coal was reached. The resulting pressure decay curves recorded for different grain size fractions of the coal were then evaluated to provide parameters on the gas sorption rate.

RESULTS

A total of 20 sorption kinetic experiments were performed with methane and CO₂, respectively on dry and moist samples of the Silesia 315 LW 155 coal. Measurements on the dry coal were conducted at 45°C for CH₄ and CO₂ on six different grain size fractions. Furthermore, experiments on moist samples were performed at the same temperature on three grain size fractions with CO₂ and CH₄, respectively. Finally, for comparison, one CO₂ and one CH₄ sorption experiment was conducted, respectively, on the dry coal at 32°C. Sorption equilibration was monitored at three to ten different pressure levels.

Dependence of sorption rate on particle size

The normalised sorption equilibration curves for the first pressure step on different grain size fractions of the dry Silesia coal are shown in Figure 2 and Figure 3 for methane and carbon dioxide, respectively. As expected, sorption equilibrium is reached fastest for the smallest grain size fraction and slowest for larger particle sizes. For methane, equilibration times are between ~6 hours for the largest grain size fraction and ~1 hour for the smallest grain size fraction, respectively. Experiments with CO₂ show similar trends but significantly shorter equilibration times of ~2 hours for the largest grain size fraction and ~0.5 hours for the smallest fraction. Direct comparison of the normalised sorption equilibration curves for CO₂ and CH₄ in Figure 4 reveals the relative rates of equilibration for the two gases. From this diagram it is evident that, sorption equilibration consistently proceeds significantly faster for CO₂ than for methane; all CO₂ curves show a more rapid decay than the corresponding methane equilibration curves.

Temperature dependence of sorption rate

A comparison of sorption equilibration curves (first pressure step) recorded at 32°C and 45°C demonstrated that pressure equilibration is reached fastest for the experiment performed at 45°C for both gases, CO₂ and CH₄. For this grain size fraction (707-2000 µm), equilibration times for CH₄ and
CO₂ at 45°C are ~10 hours and one hour, respectively, whereas equilibration times time until pressure becomes stable) for the 32°C measurements are ~18 hours and 2 hours for CH₄ and CO₂, respectively.

**Gas sorption rates on dry and moist coal**

A comparison of sorption equilibration curves for dry and moisture-equilibrated coal (grain size fraction 707–2000 µm) is shown in Figure 5 and Figure 6 for methane and carbon dioxide, respectively. For both gases, the sorption equilibration curves measured with the dry samples show a much steeper decline, i.e., much shorter equilibration times than those obtained with the moist samples. Equilibration times for CH₄ on this grain size fraction were ~45 hours and ~8 hours for experiments on the moist and the dry sample, respectively. For the moist sample it is obvious that equilibrium may not even have been reached during this time period.

For the CO₂ sorption kinetic experiments, pressure decline curves on dry and moist Silesia coal indicate that equilibration times have been sufficient. Here, equilibrium was reached after ~2 hours for the dry and ~8 hours for the moist coal experiment.

**INTERPRETATION OF EXPERIMENTAL DATA**

**Single-step model (unipore model)**

Various approaches have been used by different authors to describe the kinetics of gas sorption on coals and to link this information with models of the pore structure of coals. The present work has produced a large amount of experimental sorption kinetic data under conditions considered to be relevant for CBM production and CO₂ storage in coal seams. In order to make these results readily applicable for prediction and modeling purposes, it was attempted to parameterize the experimental equilibration curves in terms of simple, empirical or semi-empirical equations. These parameterized data may be used in the development of more sophisticated sorption models in the future.

The first parameterization approach involved application of a simple model for diffusion in homogeneous spherical particles (Crank, 1975). Although this method does not provide a perfect fit of the measured data it may be sufficient, as a first-order approximation, for certain purposes. Among others, Clarkson and Bustin (1999) and Smith and Williams (1984) used the unipore approach by Crank (1975, Eq. 6.20) to fit their experimental data. This model assumes a constant gas concentration at the surface of the spheres throughout the sorption process. In the experimental approach used in this study the gas concentration is not constant but decreases with time due to adsorption on the coal surface. The diffusion model applied instead assumes a sphere or a number of spheres with radius a, placed in a fixed volume where the free volume, not occupied by the particles, is V. The concentration of sorptive (gas) in the free volume is always uniform and initially C₀. The initial concentration of sorptive (gas) within the spheres is zero. Then the total amount Mₜ of gas sorbed after time t is expressed as a fraction of the corresponding quantity M∞ after infinite time by the relation (Crank, 1975, eqn. 6.30).

\[
\frac{Mₜ}{M∞} = 1 - \sum_{n=1}^{∞} \frac{6α(α + 1)\exp(-Dqₙ²t/a²)}{9 + 9α + qₙα²} \tag{1}
\]

Here qₙ are the non-zero roots of

\[
\tan qₙ = \frac{3qₙ}{3 + αqₙ²}, \tag{2}
\]

α is the ratio of the void volume V and the volume of the solid spheres, D the diffusion coefficient and t the equilibration time.

The parameter α is expressed in terms of the final fractional uptake of gas by the sphere by the relation:

\[
\frac{M∞}{VC₀} = \frac{1}{1 + α} \tag{3}
\]

Since many CBM/ECBM reservoir simulators operate with a single-step unipore diffusion model, it is considered useful to provide, in addition to more complex models, a unipore model approximation of the experimental data. Figure 7 shows an attempt to match a fractional uptake curve with the simple unipore diffusion model given in equations 4 through 6. Here the best fit of the experimental data was obtained with an effective diffusion coefficient of 7.88·10⁻¹¹ m²/s. For comparison the model curves for
diffusion coefficients of 7.88·10^{-10} to 7.88·10^{-12} m²/s, respectively, are plotted in this diagram. Though not perfect, the simple unipore diffusion model yields a first-order approximation of the experimental results. Furthermore, it can be easily implemented into existing CBM/ECBM reservoir simulators.

Two combined first order rate functions (bi-disperse model)

As shown in the previous section, a unipore diffusion model yields an approximation of the experimental sorption data but not the best fit. Generally it is found that parameterisation of gas sorption processes on coals requires at least assumption of a two-step process (cf. Siemons et al, 2003, Cui et al, 2004, Shi and Durucan, 2003). This can be envisaged to reflect the fact that transport and successive sorption in macro- and micropores, respectively, occurs at different time scales. Over the past 20 to 30 years numerous attempts have been made to model experimental sorption data by using bi-disperse diffusion models. Among these, the approach by Ruckenstein (1973) is well-known and used widely in its original or extended version. This model assumes a pore model consisting of spherical particles (macrosphere) containing microspheres of uniform size. Model equations and solutions are given elsewhere (Ruckenstein, 1973). This model was found to be inadequate to fit the experimentally derived data obtained in this study. Clarkson and Bustin (1999) and Shi and Durucan (2003) already pointed out the problems encountered by this model in fitting high-pressure adsorption/desorption data, because it assumed linear adsorption isotherms for CO₂ and CH₄. Generally sorption isotherms for coals are known to be non-linear.

Bhatia (1987) compared different sorption kinetic models and concluded that a reasonable fit with the bi-disperse model by Ruckenstein (1973) can be achieved but that the inconsistencies are due to Ruckenstein’s assumption of linear isotherms. Considering the deficiencies of the complex bi-disperse Ruckenstein model it was decided, mainly for practical purposes, to describe the gas sorption processes in terms of a linear combination of two 1st order rate functions with different rate constants.

The normalised equilibration curves were expressed in terms of the residual (unoccupied) sorption capacity, $Q_{\text{residual}}$, as a function of time:

$$ Q_{\text{residual}}(t) = \frac{P(t) - P_{\infty}}{P_0 - P_{\infty}} $$

(4)

Here $P_0$ and $P_{\infty}$ denote the initial, and final system pressures of a given pressure step, respectively, and $P(t)$ is the system pressure at time $t$.

$Q_{\text{residual}}(t)$ is then expressed by the combined 1st order rate functions:

$$ Q_{\text{residual}}(t) = Q_0^{I} \cdot \exp(-k^{I} \cdot t) + Q_0^{II} \cdot \exp(-k^{II} \cdot t) $$

(5)

where $Q_0^{I}, Q_0^{II}$ are the normalised sorption capacities with $Q_0^{I} = 1 - Q_0^{II}$, and $k^{I}, k^{II}$ are the two 1st order rate constants.

Figure 8 shows a comparison of two approaches to match the experimental pressure decline curve. The first approach based on a single 1st order rate sorption model gives only a rough approximation. When using two combined single 1st order rate functions, a very good fit of the data can be achieved.

RESULTS OF THE EVALUATIONS USING THE 1ST ORDER KINETIC MODEL

Grain-size dependence

Evaluations of the experimental data with the bi-disperse 1st order kinetic approach revealed that, for measurements on dry samples and depending on the grain size, 70 to 95 % of the CO₂ adsorption and 60 to 90 % of the CH₄ adsorption is accounted for by a rapid sorption step followed by a slow sorption step accounting for 5 to 30 % CO₂ and 10 to 40 % CH₄ sorption (Figure 9 and Figure 10). The total percentages for the moist samples diverge much more than for the dry samples: Depending on the grain size fraction, CH₄ and CO₂ adsorption for the rapid sorption accounts for 45 to 80 % and 45 to 85 %, respectively, followed by the slow sorption step accounting for 20 to 55 % of the CH₄ and 15 to 55 % of the total CO₂ sorption.

With an increase in the average grain size radius the fraction of the sorption capacity associated with the slow sorption process increases for both gases while the sorption capacity associated with the rapid sorption process decreases. This holds both for the dry and wet samples as evidenced by the
regression lines in Figure 9 and Figure 10. These regression lines have been tentatively extrapolated to the decimetre scale to cover the range of cleat spacing observed in coal seams (cm to decimetre). In a direct comparison between the moist samples and the dry samples a dramatic decrease in the sorption capacity attributed to the rapid sorption process can be observed for both gases when proceeding from small to larger grain sizes. Between grain sizes of 0.1 to 1 mm the slow sorption step accounts already for more than fifty percent of the total sorption capacity. Half-life times as characteristic parameters of the combined adsorption/diffusion processes are plotted in Figure 11 and Figure 12 as a function of grain size. As expected, for the dry samples, half-life times for sorption increase with increasing grain size for methane (rapid and slow sorption step) and for the rapid sorption process of CO₂. Quite unexpectedly, for the slow CO₂ sorption process, the half-life times show a tendency to decrease with increasing particle size. Measurements on moist samples show the same tendency (Figure 12). Generally, experiments on moist samples show longer half-life sorption times in most cases. Apart from the slow sorption process for CO₂, tendencies are quite similar to the dry samples, although, for CH₄ measurements, a steeper increase of half-life sorption times with increasing grain sizes can be observed for both processes (Figure 11).

DISCUSSION

Effect of grain size

Sorption kinetic experiments performed on six different particle size fractions, ranging from <63 µm to >2000 mm show that the sorption rate decreases with increasing grain size. The normalised pressure decay curves determined in the experiments were described here by a linear combination of two 1st order rate functions. The sorption process is thus subdivided into one rapid and one slow sorption step, each of which is attributed to a relative sorption capacity (percent of total sorption capacity in the pressure step) and a rate constant (or half-life time). These phenomenological parameters may be further interpreted in terms of individual transport mechanisms acting on different scales (cleat, macro- and micropore) or in different phases (surface phase, polymer matrix) of the coal. Even with additional experimental and analytical data interpretations along these lines would remain quite tentative and are beyond the scope of the present work. As shown in Figure 9 and Figure 10 the rapid sorption step accounts for ~70 to 95 % of the CO₂ adsorption and 60 to 90 % of the CH₄ sorption capacity. The decreasing relative sorption capacity of the rapid process with increasing grain sizes may be attributed to more complex pore structures on different scales in the larger particles, which is successively destroyed during grinding of the coal. Nandi and Walker (1975) observed similar effects of increasing diffusion parameters with decreasing grain sizes. They concluded that grinding produces additional macropores that have a positive influence on the sorption rate. Siemons et al (2003) investigated a similar set of experiments and found from their modeling approach that above a certain particle diameter (~0.5-1.0 µm) the characteristic times of the sorption process remain more or less constant. This effect is confirmed by investigations by Airey (1968) and Bertand et al (1970). They conclude from their studies that if a particle exceeds a certain size (~6 mm, Airey, 1968), increasing the size affects the diffusion coefficient only little. This is due to the fact that in larger particles transport along cracks or cleats becomes the controlling factor while the inter-cleat diffusion distances remain essentially constant. As evident from Figure 9 and Figure 10 the relative sorption capacity of the slow process approaches a maximum with increasing particle size while it tends towards a minimum value for the rapid sorption process. The corresponding half-life sorption times for the slow and rapid sorption process of CO₂ (Figure 11) and methane (Figure 12) tend to show a consistent increase with increasing average particle diameter. This holds for both, dry and moist coal samples.

Effect of moisture

Pressure equilibration curves on a dry and a moist Silesia coal particle size fraction are shown in a synoptic representation in Figure 5 (CO₂) and Figure 6 (CH₄). It is obvious that equilibration times for both gases are much longer for the moist sample. Suuberg et al (1993) propose the theory of water being a good swelling agent and therefore reducing gas diffusivities and permeabilities in coal. According to Jahne et al (1987) diffusivities of methane and CO₂ in water are very similar (in the order of 10-5 cm²/s) and hence the diffusion through water does not play a major role in the transport processes in coal. Thimons and Kassel (1973) and references therein assume an accumulation of water by multilayer adsorption and capillary condensation in the coal structure. The resulting effect would be a reduction of the pore radii and hence a reduction of gas diffusion rates.
Substantial differences are evident when comparing the relative sorption capacities of the rapid and slow sorption processes for CO₂ (Figure 10) and CH₄ (Figure 9) in the dry and the moist state as a function of particle size. For the moist samples the capacity of the slow sorption process increases rapidly and becomes dominant with larger grain sizes. Further measurements are needed to quantify this effect.

With respect to sorption half-life times, the general trends are similar to those observed for dry coal. The only difference is the general shift to higher values. This indicates that water present in the pore structure has mainly the effect of reducing the sorption rates.

**Effect of temperature**

It is generally observed that the sorption capacity for individual gases (CO₂ and CH₄) increases with a decrease in temperature (e.g. Schilling, 1965, Krooss et al. 2002). This observation was, also confirmed in the scope of the RECOPOL project (Busch et al., unpublished data). Apart from the sorption capacity, the sorption rate is also affected by temperature. This is evident from the pressure equilibration curves for CH₄ and CO₂: Equilibration times for measurements at 32°C are significantly longer due to a decrease in diffusion rates.

**Methane versus Carbon Dioxide**

Throughout this study, it was observed that CO₂ sorption rates are consistently higher by a factor of 2-3 (for moist samples by a factor of 5-6) than those for methane, when comparing single-gas sorption experiments. The fact that diffusivities of CO₂ in dry coals are higher than those of methane has already been concluded in a work of Clarkson and Bustin (1999) from experimental data and numerical calculations. Cui et al (2004) arrived at the same conclusion but rather from theoretical considerations.

Relative capacities for the rapid and slow sorption process showed the same trends for methane and carbon dioxide, for dry and moist samples. Differences became evident for the half-life sorption times of CO₂ and CH₄. For both gases (on dry and moist coal) an increase in the half-life time (decrease of rate) of the rapid sorption process was observed with increasing grain-size. In contrast to methane, the slow sorption process of CO₂ (on dry and moist coal) showed a negative relation between sorption half-life time and grain-sizes. This decrease in CO₂ half-life sorption times for the slow sorption process (dry and moist), compared to methane indicates different sorption sites for CO₂ than for methane.

From polymer science it is well known that CO₂ has a higher diffusion coefficient in polymer membranes than methane (Shieh and Chung, 1999; Xu et al, 2003). This observation is attributed to its lower kinetic diameter (CO₂: 3.3; CH₄: 3.8) and higher solubility in polymer membranes. Sorption experiments with CO₂/methane mixtures, also for the sample studied here, have shown that, particularly at low pressures (<6 MPa), methane is preferentially adsorbed with respect to CO₂ both on dry and moist coal (Busch et al 2003a,b,c). Furthermore, preferential desorption of CO₂ as compared to CH₄ has been observed during gas mixture experiments on different coals. This indicates that the sorption/desorption behaviour of gas mixtures cannot be readily derived from single-gas sorption measurements or results from polymer science, especially in the case of supercritical CO₂. The effects causing preferential or selective sorption from gas mixtures on natural coals are still poorly understood.

**Upscaling from laboratory to reservoir scale?**

In combination with the sorption kinetic experimental data the simple modeling approach used in this study provides a first step for the implementation of sorption kinetics into CBM/ECBM reservoir simulators and to extrapolate from small (laboratory) to large (reservoir) scale. It has been shown in the modeling part of the paper, that a rough approximation of transport parameters can be achieved by using the unipore model although a reasonable fit of the experimental data can not be achieved.

By use of a simple, semi-empirical model involving two combined 1st order rate functions, a perfect fit of the experimental data could be obtained for all different experimental conditions presented in this study. In contrast to more complex models for gas diffusion in bi-disperse pore systems of coals (e.g. Ruckenstein 1971; Clarkson and Bustin, 1999), this model does not make any assumptions concerning the structural properties of coals but uses a phenomenological description in terms of two different sorption rates ascribed to two different characteristic times for the whole sorption process. Taking the half-life sorption time and the relative sorption capacities (percentage of total sorption capacity) for the two identified sorption processes (rapid and slow) as parameterisation approaches, it was found that the relative sorption capacities for the two processes appear to have an asymptotic
behaviour tending towards a maximum value for the relative sorption capacity of the slow process and a minimum for the rapid sorption process for both gases (CO₂ and CH₄). The linear trends of the half-life sorption times vs. grain-size in the semi-logarithmic plots over two orders of magnitude led to the conclusion that this trend could be extrapolated to reservoir conditions (cleat spacing on the centimetre to decimetre scale). However, preliminary results on even larger grain size fractions (up to 8000 µm) showed erratic reductions in the characteristic sorption half-life times as well as in the sorption capacities. These results have been tentatively attributed to the augmented occurrence of cleat surfaces that might be mylonitised or mineralised, leading to the mentioned reductions in the transport and sorption properties.

In summary, the extrapolation may provide a basis for preliminary use in CBM and ECBM reservoir simulators but further work on the kinetics of sorption/desorption of methane and CO₂ on natural coals is definitely required.

CONCLUSION

In this study an extensive data-base has been used to show

- qualitative differences in the characteristic times for equilibrium sorption
- an approximation of transport parameters by use of a unipore model given by Crank (1975) and
- a simple, semi-empirical approach of fitting the experimental data by use of two combined 1st order rate functions.

The experimental studies on gas sorption on natural coals have provided unique and unexpected evidence documenting the complexity of the processes involved. Further systematic compilation of experimental data is required to improve the understanding of the observed phenomena in a qualitative and quantitative way.

Acknowledgements:

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REFERENCES


Table 1. Calculated values with the two combined 1st order rate functions for Fraction of adsorption sites and half-life sorption sites.

<table>
<thead>
<tr>
<th></th>
<th>CH₄</th>
<th>&quot;average&quot; grain size radius</th>
<th>Fraction Adsorption Sites I</th>
<th>t₁/₂ [s]</th>
<th>Fraction Adsorption Sites II</th>
<th>t₁/₂ [s]</th>
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<tr>
<td>45°C (dry)</td>
<td></td>
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<tr>
<td>P(_ini)=33.825 bar</td>
<td>1.58E-05</td>
<td>61%</td>
<td>51.6</td>
<td>39%</td>
<td>478</td>
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<tr>
<td>P(_ini)=18.4 bar</td>
<td>2.85E-05</td>
<td>93%</td>
<td>89.3</td>
<td>7%</td>
<td>2030</td>
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<td>P(_ini)=24.4 bar</td>
<td>4.43E-05</td>
<td>79%</td>
<td>115</td>
<td>21%</td>
<td>2270</td>
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<td>P(_ini)=22.075 bar</td>
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<td>70%</td>
<td>159</td>
<td>30%</td>
<td>3780</td>
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<tr>
<td>P(_ini)=25.32 bar</td>
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<td>145</td>
<td>32%</td>
<td>2470</td>
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<tr>
<td>P(_ini)=13.175 bar</td>
<td>1.25E-03</td>
<td>64%</td>
<td>178</td>
<td>36%</td>
<td>3820</td>
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<td>45°C (moist)</td>
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<tr>
<td>P(_ini)=63.8 bar</td>
<td>4.43E-05</td>
<td>81%</td>
<td>294</td>
<td>19%</td>
<td>9650</td>
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<td>P(_ini)=31.2 bar</td>
<td>8.83E-05</td>
<td>53%</td>
<td>439</td>
<td>47%</td>
<td>7610</td>
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<tr>
<td>P(_ini)=33.00 bar</td>
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<td>43%</td>
<td>1150</td>
<td>57%</td>
<td>24800</td>
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<tr>
<td>32°C (dry)</td>
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<tr>
<td>P(_ini)=19.575 bar</td>
<td>3.23E-04</td>
<td>69%</td>
<td>233</td>
<td>31%</td>
<td>9290</td>
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<tr>
<td></td>
<td>CO₂</td>
<td>&quot;average&quot; Radius of grain size (m)</td>
<td>Fraction Adsorption Sites I</td>
<td>t₁/₂ [s]</td>
<td>Fraction Adsorption Sites II</td>
<td>t₁/₂ [s]</td>
</tr>
<tr>
<td>45°C (dry)</td>
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<tr>
<td>P(_ini)=5.8 bar</td>
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<td>79%</td>
<td>46</td>
<td>21%</td>
<td>11800</td>
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<td>7.17</td>
<td>5%</td>
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<td>74.2</td>
<td>4%</td>
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<td>88%</td>
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<td></td>
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<tr>
<td>P(_ini)=9.6 bar</td>
<td>3.23E-04</td>
<td>86%</td>
<td>86.0</td>
<td>14%</td>
<td>585</td>
<td></td>
</tr>
<tr>
<td>P(_ini)=5.75 bar</td>
<td>1.25E-03</td>
<td>78%</td>
<td>120</td>
<td>22%</td>
<td>3070</td>
<td></td>
</tr>
<tr>
<td>45°C (wet)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(_ini)=15.925 bar</td>
<td>4.43E-05</td>
<td>86%</td>
<td>114</td>
<td>14%</td>
<td>7670</td>
<td></td>
</tr>
<tr>
<td>P(_ini)=17.375 bar</td>
<td>8.83E-05</td>
<td>58%</td>
<td>78.8</td>
<td>42%</td>
<td>1160</td>
<td></td>
</tr>
<tr>
<td>P(_ini)=14.35 bar</td>
<td>3.23E-04</td>
<td>47%</td>
<td>156</td>
<td>53%</td>
<td>2850</td>
<td></td>
</tr>
<tr>
<td>32°C (dry)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(_ini)=6.25 bar 32°C</td>
<td>3.23E-04</td>
<td>83%</td>
<td>64.1</td>
<td>17%</td>
<td>691</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1: Schematic diagram of the experimental set-up for single component gas adsorption on coals (A) and definitions for the volumetric method for gas sorption measurements (B).
Figure 2. Comparison of normalised CH₄ sorption equilibration curves for different grain size fractions of Silesia 315 coal (dry state).

Figure 3. Comparison of normalised CO₂ sorption equilibration curves for different grain size fractions of Silesia 315 coal (dry state).

Figure 4. Comparison of CO₂ and CH₄ pressure equilibration curves on the >2 mm fraction of the Silesia 315 coal (dry state) for two different pressure levels.
Figure 5. Comparison of equilibration times for CH₄, performed on wet and dry coal of the same grain size fraction (707-2000 µm).

Figure 6. Comparison of equilibration times for CO₂, performed on wet and dry coal of the same grain size fraction (707-2000 µm).

Figure 7. Fitting of experimental sorption rate data using a single-step or unipore model approach.
Figure 8. Comparison of the fitting of an experimental pressure decline curve with a single 1<sup>st</sup> order rate function and with two combined single 1<sup>st</sup> order rate functions.

Figure 9: Normalised sorption capacity versus average radius of grain size fraction for CH<sub>4</sub> on dry (regression in solid lines) and moist (regression in dashed lines) samples, performed at 45°C.

Figure 10. Normalised sorption capacity versus average radius of grain size fraction for CO<sub>2</sub> on dry (regression in solid lines) and moist (regression in dashed lines) samples, performed at 45°C.
Figure 11. Half-life sorption times versus grain size for CH₄ on dry (regression in solid lines) and moist (regression in dashed lines) Silesia coal, performed at 45°C.

Figure 12. Half-life sorption times versus grain size for CO₂ on dry (regression in solid lines) and moist (regression in solid lines) Silesia coal, performed at 45°C.