



Methane and CO₂ sorption and desorption measurements on dry Argonne premium coals: pure components and mixtures

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Abstract

Sorption and desorption behaviour of methane, carbon dioxide, and mixtures of the two gases has been studied on a set of well-characterised coals from the Argonne Premium Coal Programme. The coal samples cover a maturity range from 0.25% to 1.68% vitrinite reflectance. The maceral compositions were dominated by vitrinite (85% to 91%). Inertinite contents ranged from 8% to 11% and liptinite contents around 1% with one exception (Illinois coal, 5%). All sorption experiments were performed on powdered (–100 mesh), dry coal samples.

Single component sorption/desorption measurements were carried out at 22 °C up to final pressures around 51 bar (5.1 MPa) for CO₂ (subcritical state) and 110 bar (11 MPa) for methane.

The ratios of the final sorption capacities for pure CO₂ and methane (in molar units) on the five coal samples vary between 1.15 and 3.16. The lowest ratio (1.15) was found for the North Dakota Beulah-Zap lignite (VR_r = 0.25%) and the highest ratios (2.7 and 3.16) were encountered for the low-rank coals (VR_r 0.32% and 0.48%) while the ratio decreases to 1.6–1.7 for the highest rank coals in this series.

Desorption isotherms for CH₄ and CO₂ were measured immediately after the corresponding sorption isotherms. They generally lie above the sorption isotherms. The degree of hysteresis, i.e. deviation of sorption and desorption isotherms, varies and shows no dependence on coal rank.

Adsorption tests with CH₄/CO₂ mixtures were conducted to study the degree of preferential sorption of these two gases on coals of different rank. These experiments were performed on dry coals at 45 °C and pressures up to 180 bar (18 MPa). For the highest rank samples of this sequence preferential sorption behaviour was “as expected”, i.e. preferential adsorption of CO₂ and preferential desorption of CH₄ were observed. For the low rank samples, however, preferential adsorption of CH₄ was found in the low pressure range and preferential desorption of CO₂ over the entire pressure range.

Follow-up tests for single gas CO₂ sorption measurements consistently showed a significant increase in sorption capacity for re-runs on the same sample. This phenomenon could be due to extraction of volatile coal components by CO₂ in the first experiment. Reproducibility tests with methane and CO₂ using fresh sample material in each experiment did not show this effect.
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1. Introduction

In 2002 the U.S. Department of Energy (U.S. DOE) initiated a round robin study on CO₂ adsorption on a set of five samples from the Argonne Premium Coal Sample Programme (Vorres, 1990). The participating laboratories were requested to measure CO₂-adsorption isotherms on the dispatched samples in the dry state at a temperature of 22 °C and at pressures up to 60 bar (6 MPa). The complete results of this round robin study will be published by the U.S. DOE (Goodman et al., in preparation).

In addition to the measurements requested for the round-robin study, high-pressure CH₄ single-gas isotherms were measured in our laboratory at the same temperature (22 °C). Furthermore, high-pressure sorption measurements with CO₂/CH₄ mixtures were performed at a temperature of 45 °C up to pressures of ~ 180 bar (~ 18 MPa).

The objective of these additional measurements was to compare single-gas sorption isotherms (CO₂, CH₄) for well-characterised coals of different ranks as well as to study the preferential sorption behaviour from gas mixtures (CH₄/CO₂) over a large pressure range.

In the context of the EU RECOPOl-project (<http://www.nitg.tno.nl/recopol/>) our group is presently investigating the preferential sorption behaviour of gases on Carboniferous coals from the Central European Coal Basin. Experiments conducted in this context have provided evidence that although, as commonly expected, CO₂ is adsorbed preferentially to methane in most instances, preferential sorption of methane is observed for specific coals under certain conditions. Similarly, it was found in desorption experiments that while methane is mostly released preferentially to CO₂ the opposite, i.e. a preferential desorption of CO₂, may be the case in some instances (Krooss et al., 2002a; Busch et al., 2003). The sorption experiments with CO₂/CH₄ gas mixtures on the Argonne premium coals were conducted to provide experimental evidence on the preferential adsorption and desorption over a large maturity range (vitrinite reflectance: 0.25–1.68%).

Over recent years, the issues of CO₂ storage and enhanced coalbed methane recovery (CO₂-ECBM) have been addressed in numerous publications (e.g. Puri, 1990; Reeves, 2002). Many of these publications reiterate that CO₂ adsorbs in relation to CH₄ with a

ratio of 2:1 and CH₄ is readily desorbed from the coal and replaced by CO₂. The purpose of this experimental work was to verify these statements, to extend the existing data base on high-pressure gas (CO₂ and CH₄) adsorption on coals, and to contribute to a better understanding of the processes involved.

One key parameter in the investigation of CO₂ storage in coals and enhanced coalbed methane (ECBM) recovery is the relative affinity of different gas species in a mixture to the sorbent under given pressure and temperature conditions. Because the excess sorption capacity of coals for CO₂ is generally higher than the sorption capacity for methane there appears to be a general expectation that CO₂ is also preferentially adsorbed from methane/CO₂ mixtures under competitive sorption conditions. Sorption tests on Dutch coal samples with gas mixtures have indicated, however, that both preferential adsorption of CH₄ or CO₂ may occur depending on the coal composition, moisture content, and pressure and temperature conditions (Krooss et al., 2002b). To substantiate these findings, gas-mixture adsorption experiments were carried out on dry Argonne premium coals.

1.1. Samples

The Argonne Premium Coal Sample Programme consists of a selection of eight U.S. coals of different ranks ranging from 0.25% up to 1.68% VR_r. The coals have been characterised comprehensively and have been used as standard and reference samples in numerous studies. The five Carboniferous (Pennsylvanian) and Tertiary coals used for this investigation

Table 1
Argonne premium coal samples used for adsorption/desorption experiments

	Beulah-Zap	Wyodak	Illinois #6	Upper Freeport	Pocahontas #3
VR _r (%)	0.25	0.32	0.46	1.16	1.68
Rank	lignite	subbit.	hvlb.	mvlb	lvb
Liptinite (%)	–	<1	5	1	1
Vitrinite (%)	–	89	85	91	89
Inertinite (%)	–	11	10	8	10
Ash (%)	9.72	8.77	15.48	13.18	4.77
H ₂ O (%)	32.24	28.09	7.97	1.13	0.65
VM (%)	44.94	44.73	40.05	27.45	18.6

Volatile matter and ash are calculated on a dry basis. All data adopted from Vorres (1990).

have similar vitrinite contents ranging from 85% to 91% (Vorres, 1990). The maceral compositions of all five coals are very similar and dominated by vitrinite. Table 1 lists the Argonne premium coals used for gas adsorption measurements in this study and the corresponding coal petrographic information.

2. Experimental

2.1. Sample preparation

The samples were supplied in small sealed glass vials under an inert gas atmosphere. Each vial contained about 5 g of coal. The grain size of the samples was –100 mesh (–0.15 mm). After opening the glass vials the samples were transferred immediately into the stainless-steel measuring cells which were then sealed and evacuated for at least 36 h at 80 °C. This procedure was used to ensure that the samples were completely dry and that any adsorbed gas was completely removed from the coal matrix. Comparison of the round-robin results of the participating groups indicates that for two of the coal samples (Wyodak, Beulah-Zap) with very high moisture contents (28% and 32%, respectively) this procedure may not have been sufficient to achieve complete dryness (Goodman et al., in preparation).

2.2. Experimental procedure

Single-gas sorption experiments were performed at 22 °C (295.15 K). At this temperature CO₂ is in the subcritical state (T_c : 304.1 K; P_c : 7.38 MPa). The measuring cell was placed in a thermostated water bath with a relative uncertainty in temperature of less than 0.1 °C. Mixed-gas sorption experiments were performed at elevated pressures (45 °C, supercritical CO₂-conditions) in a thermostated oven (relative uncertainty in temperature <0.1 °C).

Fig. 1 shows a schematic diagram of 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 250 bar; 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

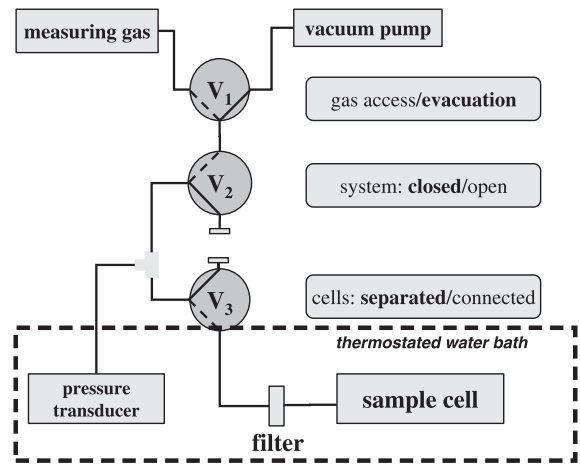


Fig. 1. Schematic diagram of the experimental setup for gas adsorption on coals.

sion in a calibration run. The coal samples are kept in a stainless-steel sample cell with a calibrated volume. A 2- μ m in-line filter is used to prevent coal or mineral particles from entering the valves.

2.3. Volumetric method for single-gas sorption measurements on coal

The volumetric method for the assessment of gas sorption on coals used in this study is outlined below with reference to the schematic flow diagram shown in Fig. 2. Here the volumes are denoted as follows:

reference volume : V_{ref}

sample cell volume : $V_{sample\ cell} = V_{sample} + V_{void}$ (1)

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 adsorption experiments this is no longer the case. Taking explicitly into account the volume of the sorbed phase, one can write:

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

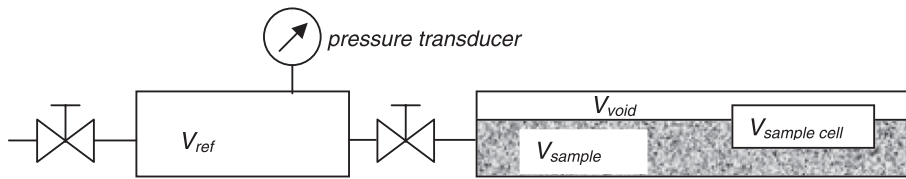


Fig. 2. Schematic flow diagram for the volumetric method for gas sorption measurement.

The corresponding evaluation requires information or estimation on the density of the sorbed phase and results in the “absolute 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). In the present work no attempt has been made to compute absolute sorption values.

2.4. Conduction of adsorption experiments

Before the start of an adsorption experiment, the void volume of the sample cell (V_{void}), i.e. the volume not occupied by the sorbent, is determined volumetrically using a non-adsorbing gas (helium). With the volume of the measuring cell known from the previous calibration measurement this measurement yields also the volume of the sorbent (V_{sample}) (cf. Fig. 2).

Volumetric gas adsorption experiments are conducted in a programmed mode. At the beginning of the experiment both the sample cell and the reference cell are evacuated to establish a defined starting

condition. The two cells are then separated by closing the shut-off valve (V_3 in Fig. 1).

In the next step, a certain amount of gas is admitted to the reference volume by opening the gas access valve (V_2 in Fig. 1). After closing this valve, a certain time (c. 1 min) is allowed for pressure and temperature equilibration in the reference cell. Using an equation of state (EOS), the amount of substance (moles of gas) in the reference cell can be computed from the pressure, the temperature and the volume of the cell. The switching valve (V_3) between the cells is then opened and the sorbate gas is admitted to the sample cell. In order to monitor the establishment of sorption equilibrium, several pressure measurements are taken at time intervals ranging between 1 and 20 min. A series of pressure measurements from an adsorption experiment is shown in Fig. 3. The high pressure peaks represent the “filling” pressures of the reference volume. When the reference volume is connected with the sample cell the pressure drops and equilibrium pressure is usually reached with the second data-point, corresponding to an equilibration

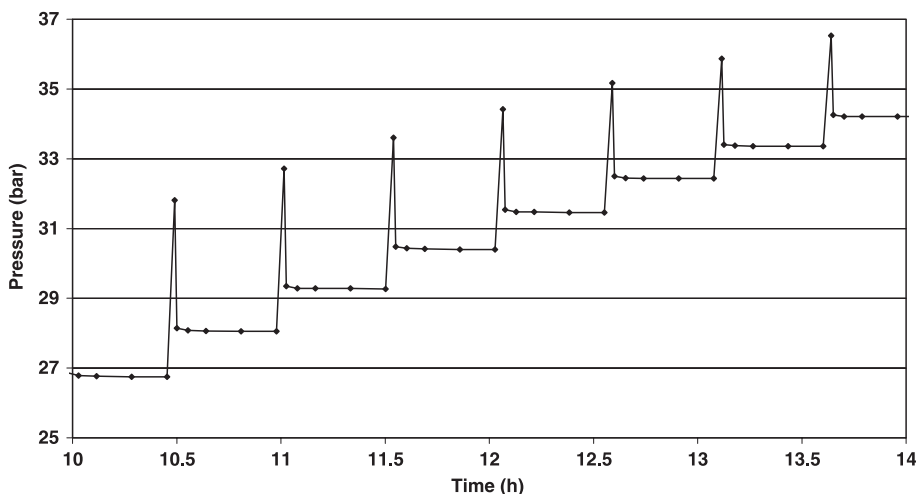


Fig. 3. Monitoring the establishment of sorption equilibrium during individual pressure steps.

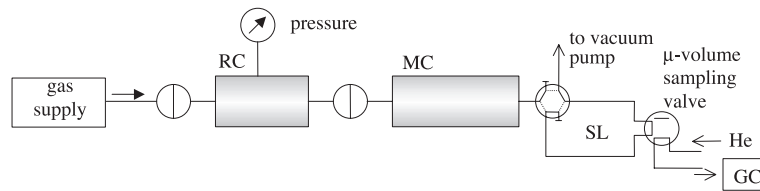


Fig. 4. Simplified scheme of the experimental set-up for measuring preferential adsorption from gas mixtures.

time of approximately 15 min. After pressure equilibration the system pressure is recorded and the cells are separated again. These steps are repeated until the final pressure level is reached.

The cumulative quantity of gas introduced through the reference cell into the previously evacuated sample cell can be readily evaluated from the experimental data by summing up the quantities introduced in each pressure step.

2.4.1. Equations of state

In the course of this study a program package provided by the *Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum* (courtesy of Prof. W. Wagner) was used. This program package is based on an EOS for methane developed by [Setzmann and Wagner \(1991\)](#) and an EOS for CO₂ by [Span and Wagner \(1996\)](#).

The EOS by [Span and Wagner \(1996\)](#) was used throughout this work because it is considered as the most reliable EOS, being based on the latest and most comprehensive sets of experimental data.

2.4.2. Calculation of Langmuir isotherms

The Langmuir sorption isotherm for monomolecular adsorption is given by:

$$\theta = \frac{m_{\text{ads}}}{m_{\infty}} = \frac{P}{K_L + P} \quad \text{where: } K_L \equiv \frac{k_d}{k_a} \quad (3)$$

Here the variables are defined as follows:

θ = fraction of occupied adsorption sites

$$\left(\frac{n_{\text{occupied}}/g(\text{sorbent})}{n_{\text{total}}/g(\text{sorbent})} \right) \quad (4)$$

$$= \frac{m_{\text{ads}}}{m_{\infty}} \left(\frac{m_{\text{adsorbed}}/g(\text{sorbent})}{m_{\text{complete saturation}}/g(\text{sorbent})} \right) \quad (5)$$

(actual mass adsorbed/mass adsorbed at complete occupation); P = pressure at sorbate gas; k_a and k_d are the rate constants for adsorption and desorption, respectively.

The Langmuir parameters (K_L and m_{∞}) were determined from the experimental data by a least-squares fitting procedure.

2.5. Preferential sorption measurements with gas mixtures

The adsorption measurements with CH₄/CO₂ mixtures require an additional analysis step to determine the relative concentrations of the two compounds in the free (non-adsorbed) gas phase. The corresponding experimental set-up consists of a flow-through measuring cell which is connected to a sample loop via a multiport valve. Free gas from the measuring cell is expanded into a previously evacuated sample loop. A small amount of this gas is then transferred to a gas chromatograph (GC) via a micro-volume sampling valve and analysed for its CH₄ and CO₂ content by a thermal conductivity detector (TCD). A simplified scheme of the set-up is shown in [Fig. 4](#). In order to assess the source gas composition and to check for compositional fractionation effects due to gas transfer and expansion, blind experiments with an empty sample cell were conducted over the entire pressure range.

3. Results

The three sets of experiments (single component CO₂ and CH₄, and gas mixture adsorption) conducted in this study are listed in [Tables 2 and 5](#) with the corresponding experimental conditions.

Table 2

Overview of sorption measurements conducted on Argonne premium coal samples with single gases (CO_2 , CH_4) at 22 °C

Coal	No. of measurements	Max. excess sorption capacity (mmol CO_2/g coal) (pressure (bar))
CO_2		
Beulah-Zap	2	Exp. 1: 1.30 (42.72) Exp. 2: 1.63 (46.99)
Wyodak	2	Exp. 1: 1.32 (40.54) Exp. 2: 1.54 (50.50)
Illinois #6	2	Exp. 1: 2.12 (44.96) Exp. 2: 2.31 (45.87)
Upper Freeport	3	Exp. 1: 1.05 (46.16) Exp. 2: 1.18 (47.04) Exp. 3: 1.13 (50.85)
Pocahontas #3	2	Exp. 1: 1.34 (46.96) Exp. 2: 1.32 (36.00)
CH_4		
Beulah-Zap	1	Exp. 1: 2.39 (112.83)
Wyodak	1	Exp. 1: 0.73 (109.74)
Illinois #6	2	Exp. 1: 0.91 (110.26) Exp. 2: 0.98 (111.18)
Upper Freeport	1	Exp. 1: 0.84 (107.40)
Pocahontas #3	1	Exp. 1: 0.85 (63.89)

All adsorption data are reported on a moisture- and ash-free basis (MAF). The moisture and ash contents are listed in Table 1. The results of the individ-

ual measurements are discussed in the following sections.

3.1. Single component gas sorption measurements

3.1.1. Methane adsorption on dry coals

High-pressure methane adsorption isotherms measured for this study are summarised in Fig. 5 and Table 2. All measurements were conducted on dry coals at 22 °C. It is evident from these figures that, with the exception of the Beulah-Zap sample, all isotherms approach a saturation limit (maximum) at elevated pressures. Furthermore, it is obvious that, again with the exception of the Beulah-Zap sample, the excess sorption capacities increase systematically with increasing rank (i.e. vitrinite reflectance) up to 50 bar (5 MPa). Above this pressure no systematic order can be identified.

The Beulah-Zap sample, which has the lowest rank ($\text{VR}_r = 0.25\%$), exhibits unusual sorption behaviour: The isotherm shows a steady increase with pressure and intersects with the isotherms of the two samples with the highest rank in this sequence. At high pressures, this sample has the highest excess sorption capacity of all five samples (2.39 mmol CH_4/g coal MAF at ~ 110 bar (~ 11 MPa)).

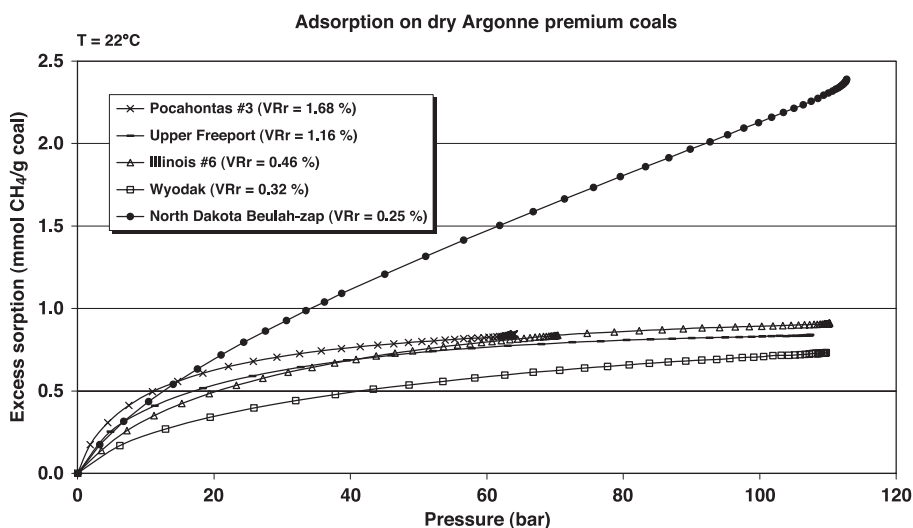


Fig. 5. Methane adsorption isotherms measured on Argonne premium coals at 22 °C.

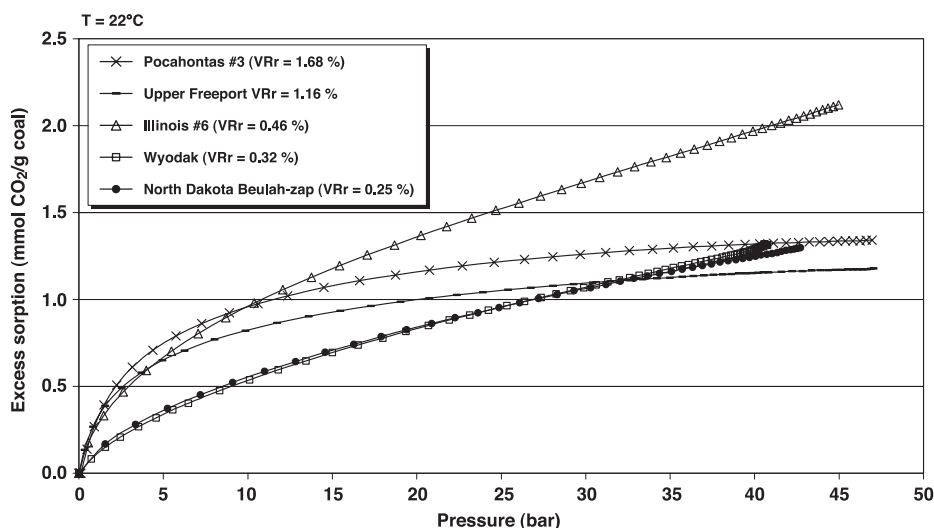


Fig. 6. CO₂ sorption isotherms measured on Argonne premium coals at 22 °C.

3.1.2. Carbon dioxide adsorption on dry coals

The results of the sorption measurements performed with CO₂ at pressures up to 51 bar (5.1 MPa) on the Argonne samples are documented in Fig. 6. The five coals show distinct differences both in the absolute values of the excess sorption capacities and in the shapes of the isotherms. Two different shapes of isotherms can be distinguished for the five samples:

- The isotherms of the low-rank coals (Beulah-Zap, Wyodak, and Illinois #6) show an almost linear increase up to the final experimental pressure, with a relatively slow increase in the low-pressure range (Wyodak and Beulah-Zap). The CO₂-sorption isotherms for the Beulah-Zap lignite and the Wyodak coal, normalised to moisture- and ash-free (MAF) material, are almost identical. Both have significantly lower excess sorption capacities (~1.3 mmol CO₂/g coal MAF) at the final pressures than the high volatile bituminous Illinois #6 coal (2.1 mmol CO₂/g coal MAF).

- The CO₂ excess sorption isotherms of the medium volatile bituminous Upper Freeport (VR_r=1.16%) and the low volatile bituminous Pocahontas #3 (VR_r=1.68%) coals show a relatively steep increase in the low-pressure range (up to 20 bar (2 MPa)) and subsequently approach limiting values of ~1.17 and ~1.35 mmol CO₂/g coal MAF, respectively, in the 40–50 bar (4–5 MPa) range.

3.1.3. Langmuir parameters for CO₂ sorption isotherms

The Langmuir parameters calculated for the CO₂-sorption isotherms of the five Argonne premium coal samples are listed in Table 3. The Langmuir coeffi-

Table 3
Langmuir parameters for CO₂ and methane sorption isotherms on Argonne premium coals

	Vitrinite reflectance (%)	Langmuir parameters	
		K_L (bar)	m_∞ (mmol/g coal MAF)
<i>CO₂</i>			
Beulah-Zap	0.25	32.15	2.24
		32.15	2.24
Wyodak	0.32	41.37	2.61
		46.33	2.89
Illinois #6	0.46	24.30	3.14
		21.39	3.26
Upper Freeport	1.16	5.37	1.17
		4.67	1.23
		4.89	1.28
Pocahontas #3	1.68	4.89	1.47
		4.50	1.46
<i>CH₄</i>			
Beulah-Zap	0.25	167.9	5.79
Wyodak	0.32	38.8	0.98
Illinois #6	0.46	24.5	1.12
		32.0	1.27
Upper Freeport	1.16	15.2	0.96
Pocahontas #3	1.68	10.7	0.98

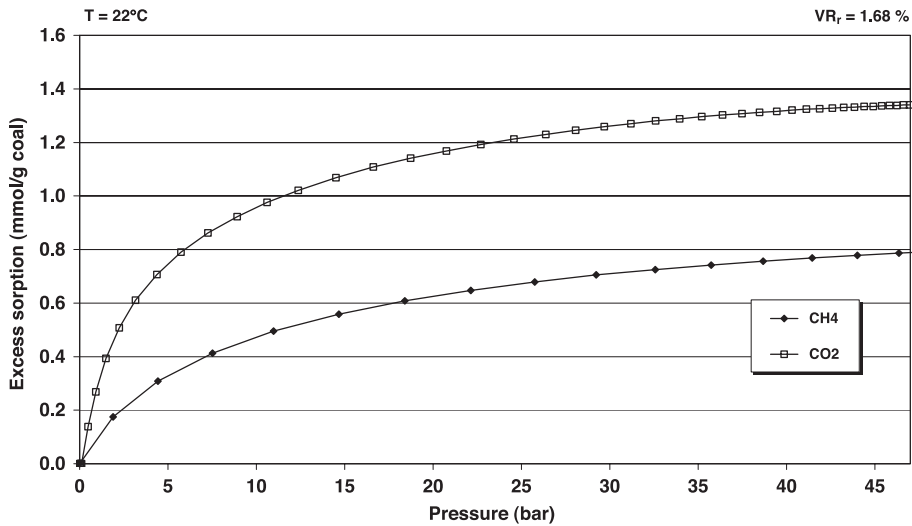


Fig. 7. Comparison of CO₂ and CH₄ isotherms of Pocahontas coal sample up to the final experimental pressure value of CO₂.

cient K_L is high (20–45 bar (2–4.5 MPa)) for the three low-mature samples and drops to values around 5 bar (0.5 MPa) for the higher rank coals. The same trend is observed for the maximum sorption (m_∞).

Langmuir parameters calculated for the CH₄ isotherms show a trend similar to the CO₂ measurements: the Langmuir coefficient K_L is again inversely proportional to the maturity of the coal and high for all samples. The Beulah-Zap lignite shows by far the

highest values for K_L (167.9 bar (16.79 MPa)) and m_∞ (5.79 mmol/g coal). Apart from this outlier the m_∞ -values are all in the range of 0.96–1.27 mmol/g coal.

3.1.4. Comparison of CO₂ and CH₄ excess sorption capacities

It is a general opinion that coal adsorbs about twice as much CO₂ as CH₄. To qualify this statement, a

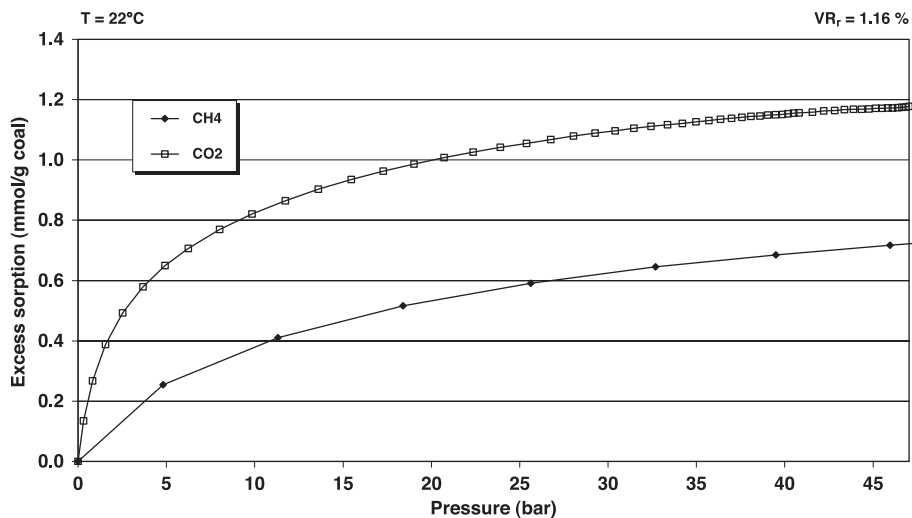


Fig. 8. Comparison of CO₂ and CH₄ isotherms of Upper Freeport coal sample up to the final experimental pressure value of CO₂.

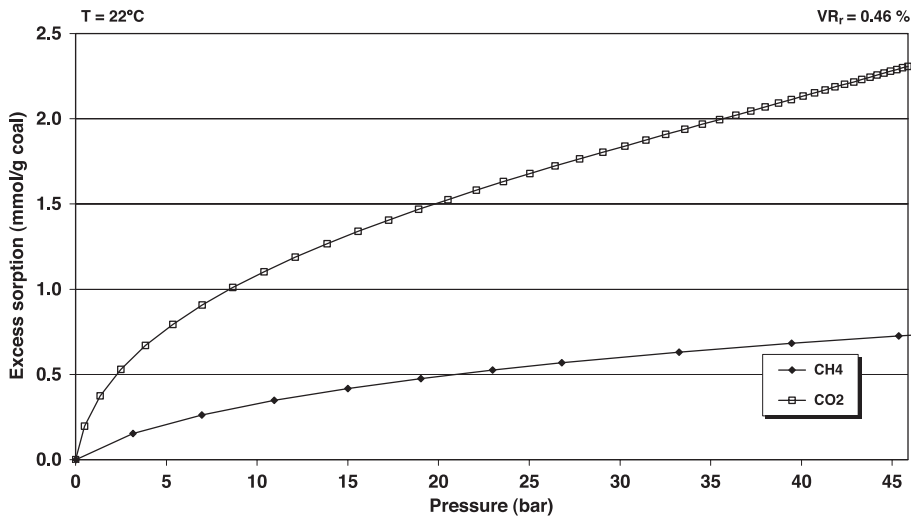


Fig. 9. Comparison of CO₂ and CH₄ isotherms of Illinois #6 coal sample up to the final experimental pressure value of CO₂.

direct comparison of CH₄ and CO₂ adsorption isotherms for each coal up to the final pressure value of CO₂ is shown in Figs. 7–11. It is evident that the molar CO₂/CH₄ excess sorption ratio is by no means constant in this set of samples. The corresponding values calculated for the maximum CO₂ pressure of the individual experiments are listed in Table 4. Within the series of samples studied here the ratios vary between values of 1.15 and 3.16. With the exception of the Beulah-Zap lignite sample (CO₂/CH₄ ratio of

1.15), there is a significant difference in the excess sorption ratio between the high rank and the low rank coals. Thus, Pocahontas #3 and Upper Freeport coals have a much lower CO₂/CH₄ excess sorption ratio (~ 1.6–1.7) than the Illinois #6 and Wyodak coals with ratios of 2.7 and 3.16, respectively.

Direct comparison of the different shapes of the isotherms shows that both CH₄- and CO₂-adsorption isotherms of the most mature coals (Pocahontas and Upper Freeport) have the same tendency to approach a

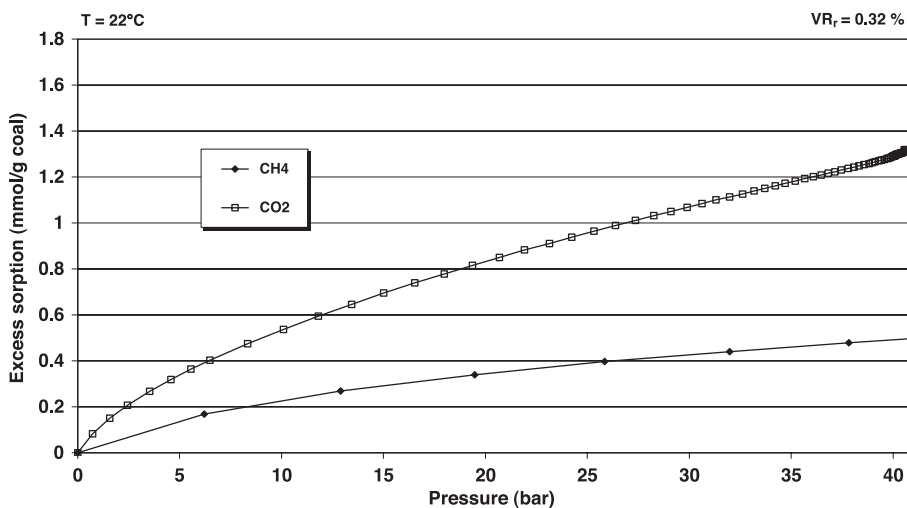


Fig. 10. Comparison of CO₂ and CH₄ isotherms of Wyodak coal sample up to the final experimental pressure value of CO₂.

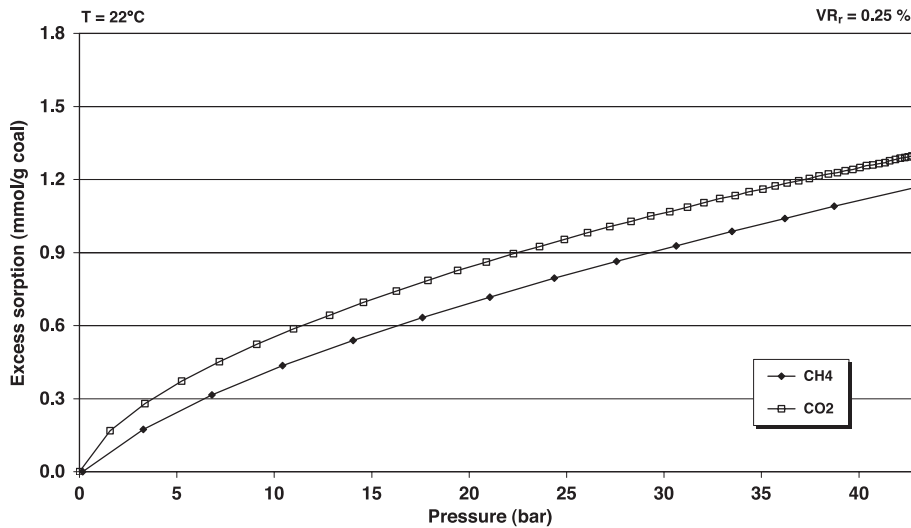


Fig. 11. Comparison of CO₂ and CH₄ isotherms of Beulah-Zap coal sample up to the final experimental pressure value of CO₂.

maximum as discussed above. For the less mature coals, especially for the Wyodak and Illinois #6 samples, there is a distinct difference in the shapes of isotherms of the two gases. Here much higher CO₂/CH₄ sorption ratios are observed for the high-pressure ranges of the isotherms.

3.1.5. Reproducibility tests

Figs. 12–14 show the results of reproducibility tests of the CO₂ and CH₄ single-component sorption experiments. The tests were conducted either as re-runs on the same coal samples after thorough evacuation and removal of adsorbed gas, or on fresh coal samples.

The follow-up test performed with Pocahontas #3 coal (Fig. 12) shows nearly identical shapes of the successively measured isotherms. In this case the measuring cell was emptied after the first experiment and refilled with a fresh coal powder sample.

Figs. 13 and 14 document two examples for follow-up tests where the same coal sample was used in a second adsorption experiment after evacuating the cell for 36 h at 80 °C. It is obvious that for the follow-up experiments slightly higher excess sorption values were achieved. Generally, follow-up experiments on the same sample resulted in excess sorption values about 5% to 15% higher than in the first experiment.

Fig. 15 shows a reproducibility test for methane adsorption on Illinois #6 coal conducted on the same charge of coal powder. The results show a good similarity in the shape and the excess sorption amounts of the two isotherms although the excess sorption of the follow-up run is slightly lower.

3.1.6. Desorption experiments

Desorption isotherms were routinely measured in all single component sorption experiments. Ideally, desorption isotherms should not deviate from the sorption isotherms. However, as evident from Fig. 16, desorption isotherms generally lie above the excess sorption isotherms, i.e. a significant hysteresis effect is associated with the sorption/desorption process. This hysteresis effect indicates that the sorbent/sorbate system is in a metastable state and at pressure decrease the gas is not readily released to the extent corresponding to the thermodynamic equilibrium val-

Table 4
Molar CO₂/CH₄ sorption ratios for Argonne premium coals of different rank

	Beulah- Zap	Wyodak	Illinois #6	Upper Freeport	Pocahontas #3
VR _r (%)	0.25	0.32	0.46	1.16	1.68
CO ₂ /CH ₄ molar sorption ratio	1.15	2.69	3.16	1.61	1.69

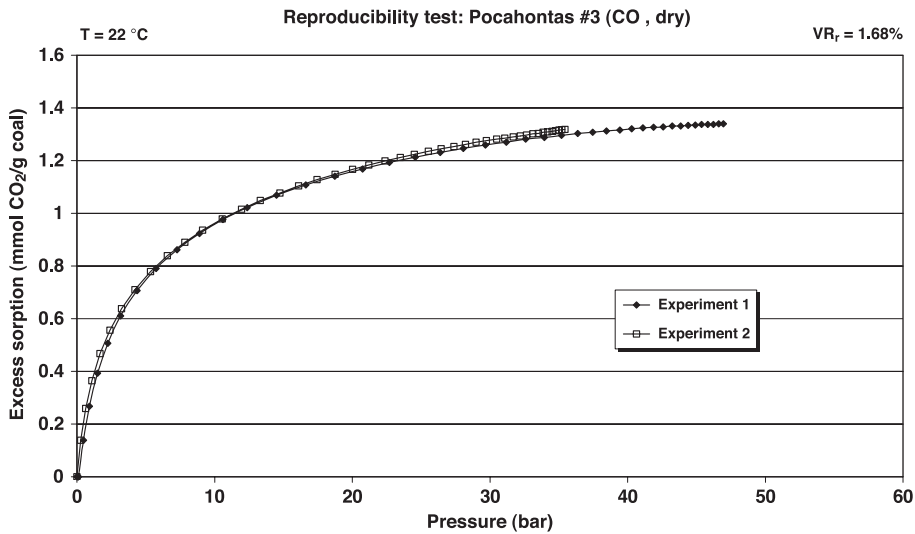


Fig. 12. CO₂-reproducibility test performed on Pocahontas #3. Fresh coal powder was used in both experiments; evacuation for 36 h at 80 °C prior to each experiment.

ue. The diagrams in Fig. 16 show that various different shapes of hysteresis trends are observed throughout the sample-set though no specific trend can be discerned with respect to maturity.

For CH₄ the Beulah-Zap (VR_r=0.25%) and Illinois #6 (VR_r=0.46%) coals show the smallest deviations between adsorption- and desorption curves

(little hysteresis), while the adsorption/desorption isotherms of the Wyodak (VR_r=0.32%) and Upper Freeport (VR_r=1.16%) exhibit a strong hysteresis particularly in the lower pressure range. The Pocahontas coal (VR_r=1.68%) takes an intermediate position. It is obvious that, with the exception of the Beulah-Zap sample, the first desorption step releases

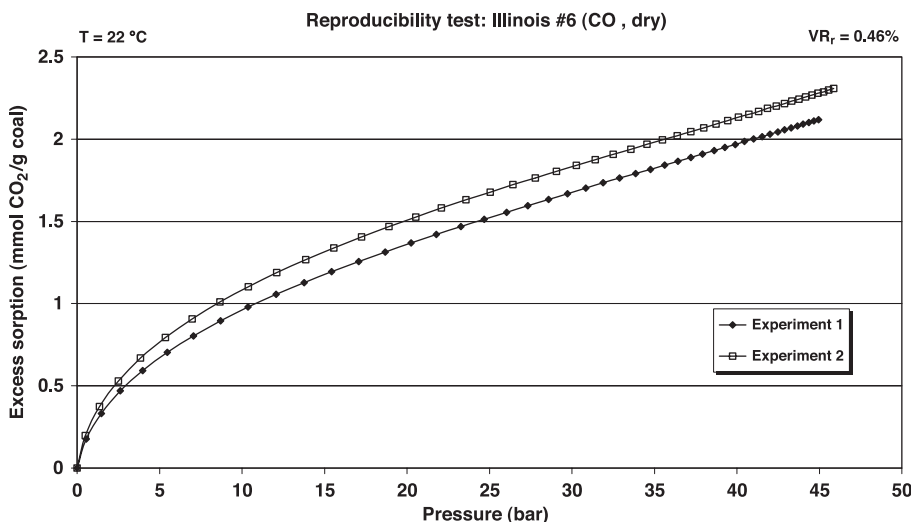


Fig. 13. CO₂-reproducibility test performed on Illinois #6. Same coal powder has been used for follow-up test after evacuation for 36 h at 80 °C.

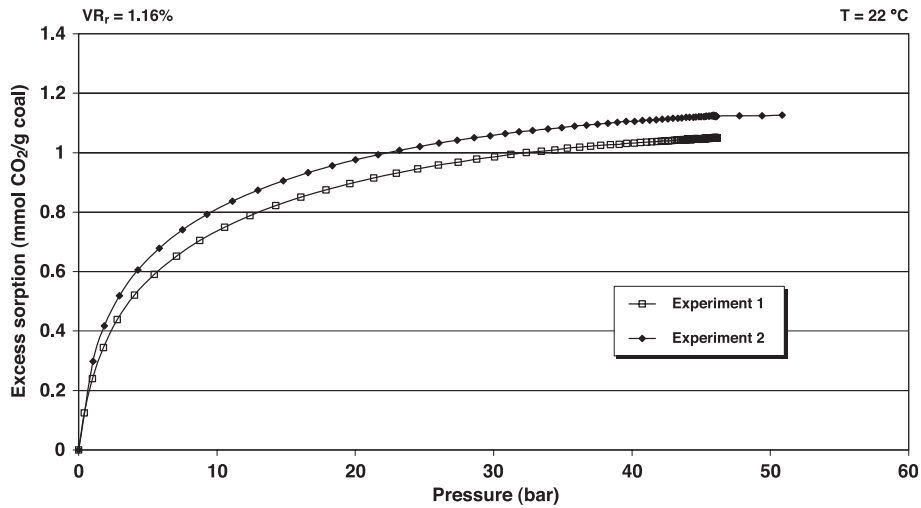


Fig. 14. CO₂-reproducibility test performed on Pennsylvania Upper Freeport. Same coal powder has been used for follow-up test after evacuation for 36 h at 80 °C.

only small quantities of CH₄ from the coal. In some instances the mass balance yields even a slight increase in excess sorption. This effect may result from small inaccuracies in the experimental values or EOS, but it could also be due to changes in the coal volume due to compressibility or swelling. For the North Dakota Beulah-Zap sample substantial release of CH₄ occurs already in the first desorption step.

Shown on the right-hand side of Fig. 16 are the combined sorption and desorption isotherms for CO₂

measured on the five Argonne coal samples. As in the case of methane the isotherms show different degrees of hysteresis. Here, relatively large deviations between the two isotherms are noticed for the two least mature samples while for the higher rank coals a closer agreement of the two curves is observed. For the Pocahontas #3 and Upper Freeport samples the first desorption steps result in an essentially zero release of CO₂, while for the three low-mature coals CO₂ desorbs directly on pressure decrease.

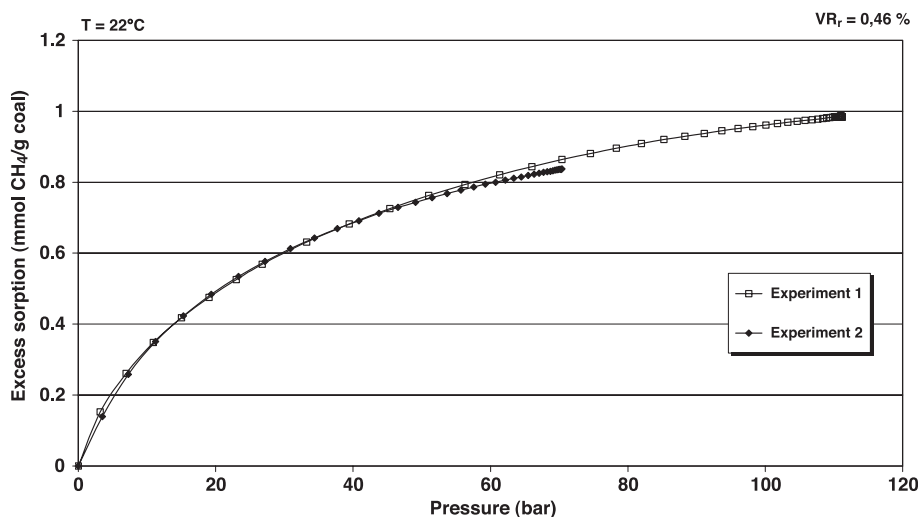


Fig. 15. CH₄-reproducibility test performed on Illinois #6. The same coal powder was used for follow-up test after evacuation for 36 h at 80 °C.

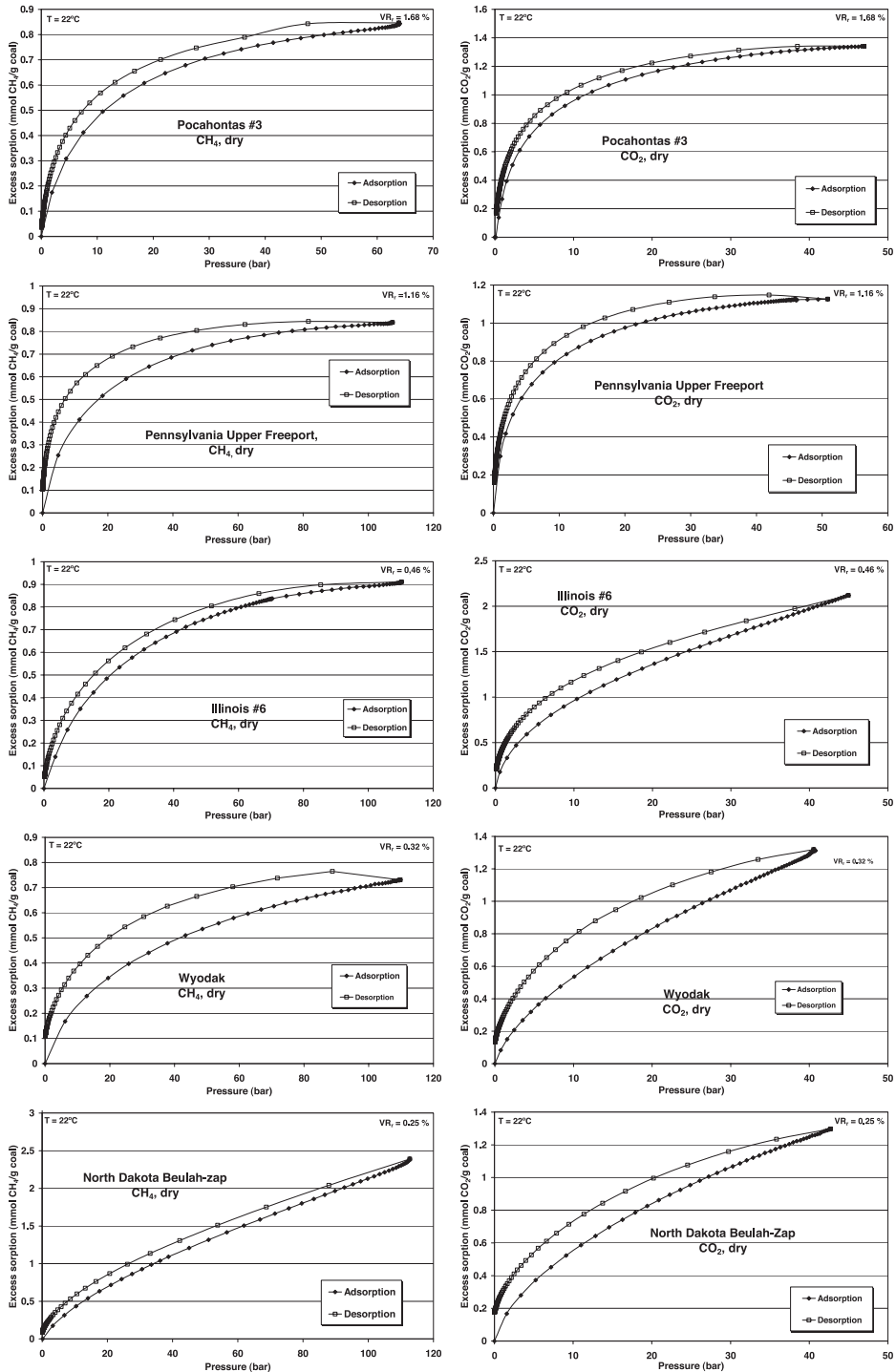


Fig. 16. Comparison of CO₂ and methane sorption and desorption isotherms for the five Argonne premium coal samples.

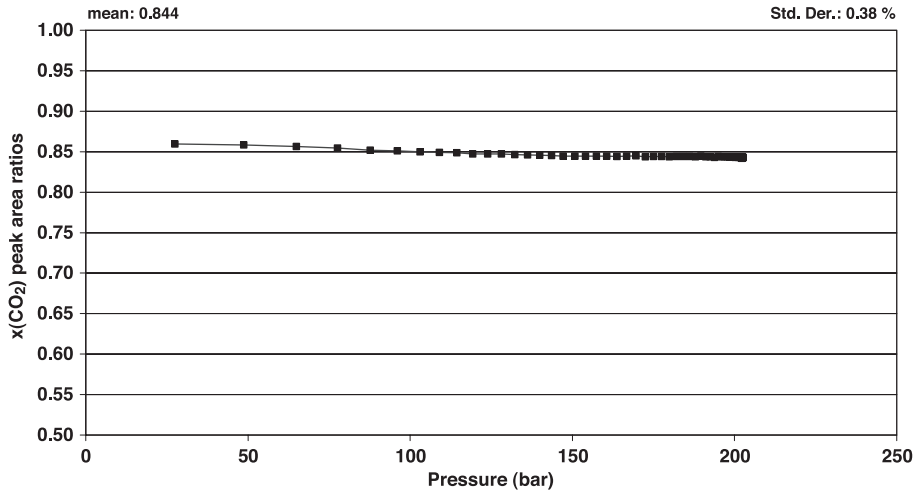


Fig. 17. Source-gas analysis performed up to 210 bar (21 MPa) at $x(\text{CO}_2)$ (peak area ratios)=0.844.

3.2. Preferential sorption measurements with CO_2/CH_4 gas mixtures

The evaluation of the experimental data was based on GC/TCD peak area ratios expressed as:

$$x(\text{CO}_2) = \frac{\text{peak area CO}_2}{\text{peak area CO}_2 + \text{peak area CH}_4} \quad (6)$$

This procedure was chosen to keep as close as possible to the raw data and avoid any distortion of the results that might be due to further processing and calibration steps (e.g. non-linearity in the detector response over large concentration ranges). In consequence the results are qualitative and aim at an unequivocal assessment of the occurrence of preferential adsorption and desorption of one of the two

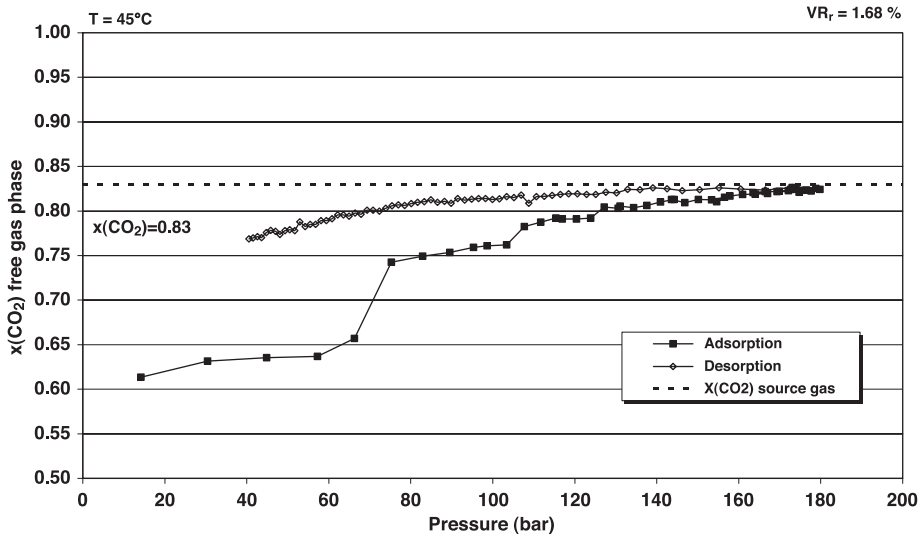


Fig. 18. High-pressure mixed-gas preferential sorption measurements on Pocahontas #3 in the dry state at 45 °C.

Table 5
Adsorption measurements conducted with gas mixtures (CH₄/CO₂)
at 45 °C on dry coal samples

Coal sample	$x(\text{CO}_2)$	P_{MAX} (bar)
Beulah-Zap	0.91	126.20
Wyodak	0.17	123.53
Illinois #6	0.84	113.05
Upper Freeport	0.79	117.78
Pocahontas #3	0.82	180.90

sample gases. Quantitative measurements involving thorough calibration procedures are under way.

3.2.1. Blind runs

The blind tests performed prior to the sorption experiments with the gas mixtures showed a small degree of fractionation resulting in slightly elevated CO₂ contents of the sampled gas at low pressures. The results of one of these tests are shown in Fig. 17. Here the measured CO₂/CH₄ peak area ratios decrease from 0.86 to 0.844 in the pressure range from 20 to 200 bar (2–20 MPa). Generally, the fractionation effects observed in the blind experiments were in the range of 1–2% and thus much smaller than the fractionation effects observed with the actual coal samples.

3.2.2. Preferential sorption tests

The results of the sorption and desorption experiments with CO₂/CH₄ gas mixtures are summarised in Figs. 18–22.

The source-gas composition $x(\text{CO}_2)$ is compared with the composition of the free gas-phase after achieving equilibrium with the coal matrix. In the diagrams the peak area ratios of the source gases used are shown as dotted lines. The $x(\text{CO}_2)$ values lower than those of the source gases indicate depletion of the free (non-adsorbed) gas phase in CO₂ while $x(\text{CO}_2)$ values above the dotted lines indicate an enrichment of the free gas-phase with respect to the source gas.

For the *adsorption* curves, $x(\text{CO}_2)$ values lower than the source gas composition represent preferential adsorption of CO₂ from the gas mixture. As a consequence, $x(\text{CO}_2)$ values of the *desorption* curves lower than those of the source gases indicate preferential desorption of CH₄ from the coal. This behaviour is considered beneficial for CO₂ deposition and CO₂-enhanced methane production from coal seams.

Source-gas compositions of 0.79–0.91 were used for four out of the five coal samples (Table 5) to ensure similar initial conditions. For the Wyodak coal a much lower CO₂/CH₄ ratio was chosen to verify if comparable tendencies would be observed when reducing the CO₂ content of the source gas with respect to CH₄.

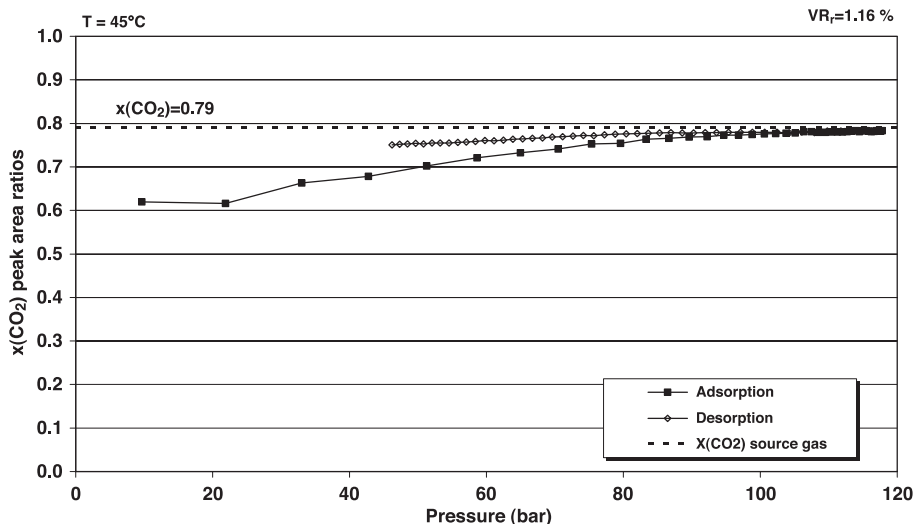


Fig. 19. High-pressure mixed-gas preferential sorption measurements on Upper Freeport in the dry state at 45 °C.

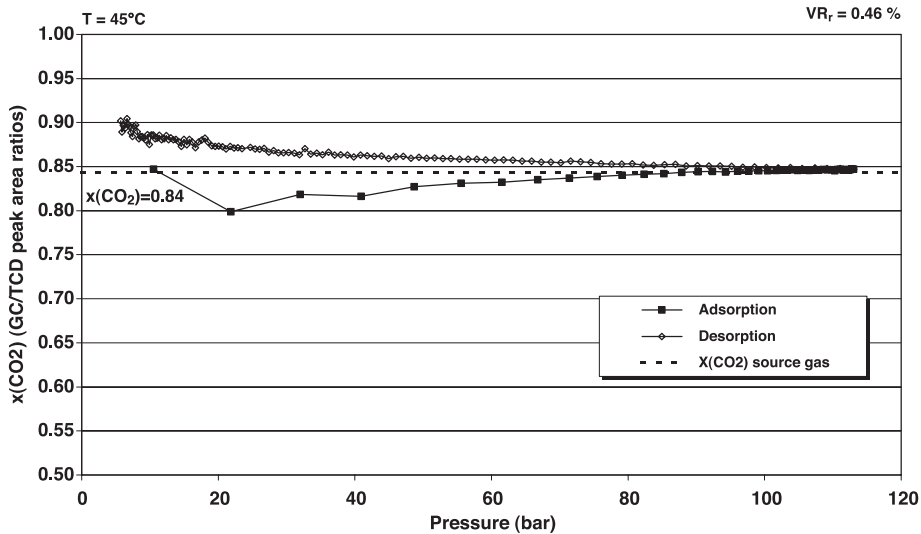


Fig. 20. High-pressure mixed-gas preferential sorption measurements on Illinois #6 in the dry state at 45 °C.

The results of the preferential sorption tests on the five coals are shown in Figs. 18–22. It is evident from these diagrams that distinct differences exist in the preferential CO_2/CH_4 sorption behaviour of the coal samples: the two highest rank coals (Upper Freeport, $\text{VR}_r = 1.16\%$ and Pocahontas #3, $\text{VR}_r = 1.68\%$) measured at very similar mixed-gas compositions of 0.79 and 0.82, respectively, exhibit a preferential sorption behaviour “as expected” (Figs. 18 and 19): preferential adsorption of CO_2 and

preferential desorption of CH_4 . In these two cases the adsorption curves show the highest degree of preferential adsorption (fractionation) with respect to the source-gas at the lowest pressure and approach the source gas composition at their final pressure levels. The desorption curves deviate less strongly from source gas composition, while preferential desorption of CH_4 increases with decreasing pressure. Preferential adsorption of CO_2 and preferential desorption of CH_4 is developed much more

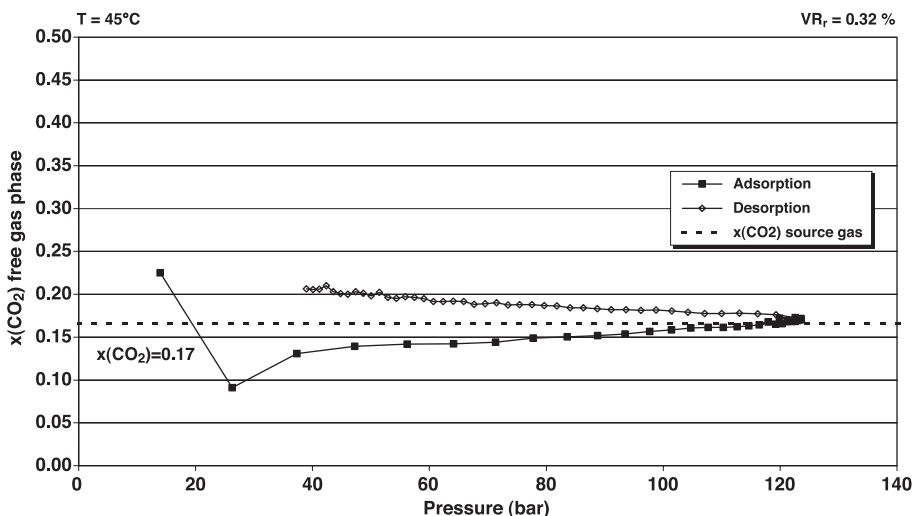


Fig. 21. High-pressure mixed-gas preferential sorption measurements on Wyodak coal in the dry state at 45 °C.

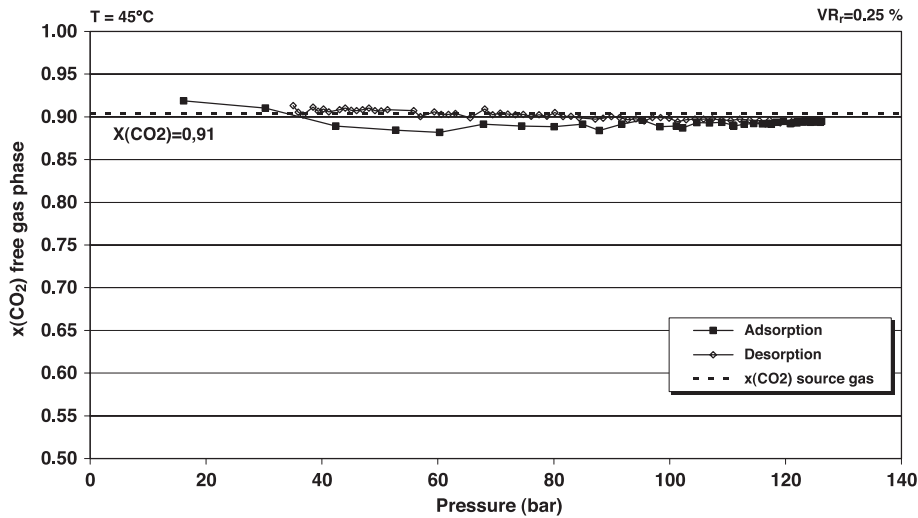


Fig. 22. High-pressure mixed-gas preferential sorption measurements on Beulah-Zap in the dry state at 45 °C.

strongly here for the more highly mature sample (Pocahontas #3).

The three Argonne coal samples of lower rank (Illinois #6, Wyodak, North Dakota Beulah-Zap; Figs. 19–22) exhibit a preferential sorption behaviour contrasting with the observations for the Pocahontas and the Pennsylvania Upper Freeport coals. All three samples show preferential desorption of CO₂ which is particularly the case for the Illinois #6 and Wyodak samples (Figs. 20 and 21) and to a lesser extent for the Beulah-Zap sample (Fig. 22). This phenomenon becomes even more obvious at lower pressures. A characteristic difference can be observed for the adsorption process as well. Evidently, all three coals show to some extent preferential adsorption of CH₄ at low pressures (between 20 and 40 bar (2–4 MPa)). This phenomenon has already been reported for other samples by Krooss et al. (2002a) and Busch et al. (2003).

4. Discussion

All of the sorption/desorption experiments with CO₂ and methane described in this study have been performed on dry coals. While this puts limits on the direct applicability to CBM, ECBM and CO₂ storage processes it avoids the additional complexity of the influence of moisture and still provides general information on the various effects and processes asso-

ciated with gas adsorption on natural coals. The Argonne premium coal sample sequence represents a well-studied sample set covering a relatively wide maturity range and similar maceral compositions. Therefore, it was ideally suited for this systematic sorption study.

4.1. Effects of rank and maceral composition on excess sorption

Within the sample set studied a general tendency can be observed of adsorption capacities up to ~ 50 bar (~ 5 MPa) increasing linearly with rank although there are some exceptions: the Beulah-Zap lignite, with the lowest rank of all samples, shows the highest methane sorption capacity in this sequence. Furthermore, the Illinois #6 coal has the highest CO₂ sorption capacity while it has the third lowest rank of all samples ($VR_r = 0.46\%$).

Laxminarayana and Crosdale (1999a) propose that maceral composition is an important control on the gas adsorption capacity. In a later contribution, Laxminarayana and Crosdale (2002) report no direct trend of increasing CH₄ adsorption capacity with total vitrinite contents. This is supported by investigations performed by Clarkson and Bustin (1999) for CH₄ and CO₂ on moist coals.

While maceral compositions vary only little in the Argonne sample set and therefore differences in

adsorption capacity cannot be addressed with respect to this attribute, the influence of the rank on gas adsorption capacity is clearly documented at least for the low pressure range. Prinz et al. (2001) support this statement and demonstrate that especially the sorption capacity of methane is strongly dependent on the rank for moist coals.

Increasing adsorption capacities are attributed to the microporous structure of the coal (Clarkson and Bustin, 1996; Lu et al., 2001). The latter ascribes the increasing capacities to an increase of the crystalline phase in the coal with decreasing amounts of volatile matter and consequently with an increase in vitrinite reflectance. This increase in crystalline phase would lead to an increase in the microporosity of the coal.

Laxminarayana and Crosdale (1999b) state a clear relationship of decreasing Langmuir pressures (K_L) with increasing rank, implying that the pore surface becomes less heterogeneous and coverage of the surface is more complete. This observation is supported by our data. The Langmuir pressures calculated for the CH_4 and CO_2 isotherms show a distinct decrease with increasing rank which is particularly large for CO_2 when proceeding from the Illinois #6 ($VR_r=0.46\%$) to the Upper Freeport ($VR_r=1.16\%$) coal. Like in most instances the Beulah-Zap lignite ($VR_r=0.25\%$) forms an exception having a very high K_L -value for CH_4 and a slightly smaller K_L -value for CO_2 isotherms than the Wyodak sample ($VR_r=0.32\%$).

4.2. Comparison of CH_4 and CO_2 excess sorption capacities

A relatively large variability was found in the ratio of the excess molar amounts of sorbed CO_2 and CH_4 , determined at the final CO_2 -pressure. The values range from 1.15 to 3.16 (Table 4) and show, apart from the Beulah-Zap lignite, a decrease with increasing rank. This behaviour appears to reflect a higher affinity of CO_2 to low rank coals.

4.3. Potential effects of CO_2 on the sorption behaviour of coals

Repetitive sorption experiments with CO_2 on the same coal samples consistently showed a slight in-

crease in sorption capacity in each successive test. A similar observation has been reported by Ohga (2002) after treatment of coal with supercritical CO_2 . On the other hand, the sorption capacity remained essentially constant in repetitive sorption tests with methane. This result is interpreted as the consequence of an extraction process or a change in the macromolecular coal structure caused by the carbon dioxide. Future research should address this phenomenon in particular with respect to sorption experiments with CO_2 in the supercritical state.

4.4. Preferential sorption phenomena

Fundamental differences were observed in the preferential sorption/desorption behaviour from CO_2/CH_4 gas mixtures by low- and high rank coals. While the expected effect of *preferential sorption of CO_2* and *preferential desorption of CH_4* was observed for the high rank coals in this series, the low-rank coals showed preferential adsorption of methane at low pressures and preferential desorption of this gas component over the whole pressure range. Preferential adsorption of CH_4 at low pressures was observed in previous experiments (Krooss et al., 2002a); however, neither a dependence on rank nor on maceral composition has been established. No references have been found as yet supporting the findings of preferential CO_2 desorption from low-rank coals.

Sorption experiments on single-gases (CO_2 and CH_4) and their binary mixtures (52.9% CH_4 , 47.1% CO_2) on coals from the Sydney Basin, Australia, performed at 30.2 °C up to 6 MPa (Crosdale, 1999) showed preferential adsorption and desorption of CH_4 by comparison of the pure end member and the pure components of the gas mixture. The authors explain this behaviour by pore filling models which assume a faster diffusion rate for CH_4 as compared to CO_2 . Preliminary results of adsorption-rate measurements with these two gases on a Polish coal at 45 °C and up to 15 MPa performed in our laboratory render this assumption questionable. In the experiments performed on six different grain size fractions sorption equilibrium was consistently reached significantly faster by CO_2 than by CH_4 . These findings rule out a kinetic effect resulting in preferential sorption of CH_4 .

5. Summary and conclusions

The study presented here provided experimental data for adsorption and desorption of carbon dioxide and methane on a set of well-characterised coals of similar maceral composition covering a maturity range from 0.25% to 1.68% vitrinite reflectance. The single component experiments were conducted over a period of a few months with the same experimental set-up under identical conditions. Each CO₂ experiment was run at least in duplicate to ensure reproducibility, and random sample reproducibility tests have been performed for the CH₄ measurements. Therefore the resulting data-sets are considered to provide a good basis for comparison of the sorption and desorption properties of coals of different rank.

The Beulah-Zap lignite, the least mature sample of this selection (VR_r=0.25%), showed a sorption/desorption behaviour that deviated in many aspects from the general trends observed for the other four samples.

For the latter samples the ratios of the molar sorption capacities for CO₂ and methane at 22 °C on the dry coals ranged between 1.7 and 3.17 with a maximum for the Illinois #6 coal (VR_r=0.46%) and a tendency to decrease with rank. The Illinois #6 sample exhibited also the highest sorption capacity for CO₂ of all samples and the second highest methane sorption capacity which was only surpassed by the extraordinarily high methane sorption capacity of the Beulah-Zap lignite.

Comparison of the adsorption and the desorption curves for the individual experiments revealed different degrees of hysteresis, which for CO₂ tended to decrease with increasing rank, while no systematic maturity-related pattern was discernible for methane. Two basic types of desorption isotherms were found. The first type shows almost no decrease in excess sorption during the first desorption steps while the second type is characterised by an immediate decrease in the excess adsorbed gas quantity upon pressure decrease. Generally, the desorption isotherms lie above the adsorption isotherms.

The extent of preferential sorption and desorption of CH₄ and CO₂ cannot be derived from single component sorption tests but requires experiments with gas mixtures. Competitive sorption from CO₂/CH₄ gas mixtures was therefore studied under well-controlled conditions to provide, in a first step,

qualitative evidence for the direction and extent of this process. In accordance with previous observations it was found that, although preferential sorption of CO₂ appears to be the regular case at high pressures, methane may be preferentially adsorbed by certain coals in the low-pressure range (up to 40 bar (4 MPa)). More importantly, for coals exhibiting preferential methane sorption, a preferential desorption of CO₂ can be observed even at high pressures. This phenomenon which, to our knowledge, has not been studied or reported previously calls for closer and systematic investigation specifically with respect to ECBM and CO₂ storage activities.

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