

## Accepted Manuscript

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PII: S0166-5162(10)00149-7  
DOI: doi: [10.1016/j.coal.2010.08.002](https://doi.org/10.1016/j.coal.2010.08.002)  
Reference: COGEL 1754

To appear in: *International Journal of Coal Geology*

Received date: 18 May 2010  
Revised date: 4 August 2010  
Accepted date: 4 August 2010



Please cite this article as: Battistutta, Elisa, van Hemert, Patrick, Lutynski, Marcin, Bruining, Hans, Wolf, Karl-Heinz, Swelling and sorption experiments on methane, nitrogen and carbon dioxide on dry Selar Cornish coal, *International Journal of Coal Geology* (2010), doi: [10.1016/j.coal.2010.08.002](https://doi.org/10.1016/j.coal.2010.08.002)

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# Swelling and sorption experiments on methane, nitrogen and carbon dioxide on dry Selar Cornish coal

Elisa Battistutta, Patrick van Hemert, Marcin Lutynski, Hans Bruining and Karl-Heinz Wolf

*Faculty of Civil Engineering and Geosciences. Department of Geotechnology. Section of Geo Science, Delft University of Technology, Stevinweg 1, 2628 CN Delft*

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## Abstract

Sorption isotherms of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> are determined at 318 K and 338 K for pressures up to 16 MPa in dry Selar Cornish coal using the manometric method. Both equilibrium sorption and desorption were measured. The desorption isotherms show that there is no hysteresis in N<sub>2</sub>, CH<sub>4</sub> sorption/desorption on coal. The time to achieve equilibrium depends on the gases and is increasing in the following order: He, N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>. The results show that the sorption ratio between the maximum in the excess sorption N<sub>2</sub>:CH<sub>4</sub>:CO<sub>2</sub> = 1:1.5:2.6 at 318 K and 1:1.5:2.0 at 338 K. Obtained ratios are within the range quoted in the literature.

Swelling and shrinkage induced by CO<sub>2</sub> injection and extraction from Selar Cornish coal have been measured. The experiments have been conducted on unconfined cubic samples using strain gauges measurements at 321 K for pressures up to 4.1 MPa. It has been found that the mechanical deformation is fully reversible.

The density of CO<sub>2</sub> in its sorbed phase, has been extrapolated from the excess sorption isotherm calculated including the swelling. The resulting value is unrealistically high. Possible reasons for this behavior are discussed in the text. Absolute sorption for CO<sub>2</sub> has been estimated considering also the change in the coal volume due to swelling. The resulting isotherm calculated with or without the swelling are almost the same.

*Keywords:* sorption, swelling, equilibration time, reversibility, absolute density

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## 1. Introduction

Concerns about global warming generated interest in reducing the emissions of the main greenhouse gas - carbon dioxide ( $\text{CO}_2$ ). Large quantities of  $\text{CO}_2$  are produced during the combustion of fossil fuels. Methods intended to reduce  $\text{CO}_2$  emission include its storage in geological formations, e.g., saline aquifers and (depleted) gas reservoirs. One of the options is  $\text{CO}_2$  injection into underground coal in combination with the production of  $\text{CH}_4$  originally present in coal seams. Another idea is to inject flue gas, i.e. a mixture of  $\text{N}_2$  and  $\text{CO}_2$  (Mazumder et al., 2006a; Reeves, 2001). In these cases  $\text{N}_2$  acts as a stripping agent. This technology is known as flue gas-Enhanced Coalbed Methane (flue gas-ECBM) recovery.

The effectiveness of enhancing methane production by  $\text{CO}_2$  and/or  $\text{N}_2$  depends on the sorption behavior of the main constituents. Therefore, knowledge about sorption behavior of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2$  is required. Many experimental dry coal-sorption studies have been published in the last years (e.g., Busch et al. (2007); Chaback et al. (1996); Clarkson and Bustin (1999b); Day et al. (2008); Gruskiewicz et al. (2009); Majewska et al. (2009); Ottiger et al. (2006); Prusty (2008); Saghafi et al. (2007); Siemons and Busch (2007)). The measurements quantify the sorption capacity of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2$  in different kinds of dry coal.

The time required for attaining thermodynamical equilibrium for the gas sorbed by the coal is an important factor in any *in situ* application. Recent literature stresses the importance of the latter as an essential factor in establishing proper excess sorption isotherms for gases (Day et al., 2008; Gruskiewicz et al., 2009; Majewska et al., 2009; Prusty, 2008). The equilibration time depends on gas, temperature of the system and the grain sizes of coal used in the experiments. A few authors studied the kinetics of the gas sorption on coal (Busch et al., 2004; Clarkson and Bustin, 1999b; Goodman et al., 2006; Gruskiewicz et al., 2009; Siemons et al., 2003; Solano-Acosta et al., 2004).  $\text{CH}_4$  and  $\text{CO}_2$  adsorption occurs much faster in fine grained fractions. Siemons (2003) reported that equilibration time is proportional to the grain size up to  $1500 \mu\text{m}$ ; above it is more or less constant. The grain size used in sorption experiments usually ranges between  $63 \mu\text{m}$  and  $2000 \mu\text{m}$  (Busch et al., 2006) with the exception of the work of Majewska (2009) who used coal blocks. Equilibration times reported by these authors vary between 1 hour to 440 hours. Mazumder (2006) in his coal measured that the cleat spacing in coal is between  $500 \mu\text{m}$  and  $5000 \mu\text{m}$ ). In order to maintain

the structural integrity of the coal, in this paper the chosen particle size is between 1.5 - 2 mm, that leads to long equilibration time.

Sorption/desorption of gases on coal induces a relevant effect on its mechanical structure: the swelling/shrinkage of the matrix. Coal swelling induced by gas adsorption is a phenomenon extensively studied either using optical systems (Robertson, 2005) or strain gauges (Levine, 1996). Literature data concerning experimental results is remarkable and results are relatively consistent amongst different laboratories (van Bergen et al., 2009; Cui et al., 2007; Day et al., 2007; Durucan et al., 2009; Levine, 1996; Mazumder and Wolf, 2007; Pini et al., 2009; Reucroft and Patel, 1986; Robertson, 2005; Shi and Durucan, 2005). CO<sub>2</sub> sorption on coal induce a bigger swelling effect on the coal matrix than CH<sub>4</sub> and N<sub>2</sub>. It has been shown that at high pressure the coal is almost saturated and no sorption and swelling are observed anymore. At pressures above 20 MPa, as the rate of change in adsorbed gas content becomes small, matrix compression dominates and can decrease the volumetric strain. (Pan and Connell, 2007).

In this study, the isotherm curves of N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> were determined at 318 K and 338 K for pressures up to 16 MPa in dry Selar Cornish coal using the manometric method (Hemert et al., 2009). The authors do not yet address mixed gas sorption but focus on pure gas (de)sorption. The chosen range is representative for *in situ* conditions. In Europe usually seams suitable for CO<sub>2</sub> storage are at depths over 500 meters, with correspondingly high reservoir pressures and temperatures (308-338 K, 6-15 MPa).

Swelling/shrinkage measurements have been conducted on Selar Cornish coal with CO<sub>2</sub> using strain gauges on unconfined cubic samples at T=321 K up to 4.1 MPa.

Excess sorption isotherms provides insufficient information for ECBM applications because it is considering the void volume that can be occupied by the gas as constant disregarding that it is reduced by the volume of the gas in its sorbed phase and by the swelling induced by the gas absorption. Therefore it is preferable to use the absolute sorption isotherm which is the total amount of gas that can be sorbed per unit mass of coal. The absolute sorption is considering also the volume occupied by the CO<sub>2</sub> in its sorbed phase. In this paper the absolute sorption has been recalculated considering also the changes in volume of the coal induced by the swelling.

In this study all the experimental results are fitted with the Langmuir model (Sakurovs et al., 2007), which adequately represents gas sorption in coal and provide values of parameters that can be used in many reservoir

simulations.

## 2. Experimental method and materials

### 2.1. Sample preparation

#### 2.1.1. Sorption measurements

All experiments are performed with a semi-anthracite, from the Selar Cornish, South Wales Coalfield (vitrinite reflectance is  $R_{max}=2.41$ ). Maceral and ash content are reported in Table 1.

For the sorption experiments the stored coal blocks are broken, crushed and then sieved. The fraction between 1.5 and 2.0 mm is used in the study. Sieving was brief in order to avoid dust production. Batches of 50 to 70 cm<sup>3</sup> are sealed and stored at about 276 K until used in the experiments. Before placing the sample in the cell, it has been dried in oven for 24 hours at 378 K under vacuum conditions in order to remove all the moisture content. After placing the sample in the cell, at the beginning of each experiment, the cell is evacuated at 322 K for at least 24 hours under vacuum conditions. The sample weights after evacuation are reported in Table 3. Table 2 shows the purity and critical constants of the gases used in this study. All gases are supplied by Linde Gas b.v. with the purities as specified in Table 2.

#### 2.1.2. Swelling measurements

For the swelling experiments coal blocks have been cut to obtain cubic samples with an average dimension of 10x10x10 cm. The selected samples are not presenting any consistent fracture, and are considered to be homogeneous. Gases have been provided by BOC Gases(UK) Ltd; purity of gases is reported in Table 2.

### 2.2. Experimental setups

#### 2.2.1. Sorption measurements

For the sorption experiments two setups were used. One of the setups, that has a higher accuracy, is extensively described in Hemert et al. (2009) and is used for the experiments with CO<sub>2</sub>. Thus, CO<sub>2</sub> sorption behavior is accurately described in the critical pressure and temperature range. Here we describe the other setup, used for N<sub>2</sub> and CH<sub>4</sub> experiments. The manometric apparatus (Fig. 1) consists of 5 stainless-steel cells: two sample cells, two reference cells and one common reservoir. Two sorption experiments can be

Table 1: Properties of the used U.K. Selar Cornish coal.

Proximate analysis				
Moisture mass-%	Vol. matter mass-% (w.f.)	Fix. Carbon mass-% (w.f.)	Ash mass-% (d.a.f.)	
0.64±0.04	9.61±0.02	85.37±0.01	4.38±0.06	
Ultimate analysis <sup>1</sup>				
Carbon mass-%	Hydrogen mass-%	Nitrogen mass-%	Sulfur mass-%	Oxygen mass-%
85.2±1.3	3.28±0.03	0.77±0.05	0.92±0.01	5.60±0.01
Microscope analysis				
R <sub>max</sub> %	Vitrinite vol-%	Liptinite vol-%	Inertinite vol-%	Minerals vol-%
2.41	73.6	24.6	0.0	1.8

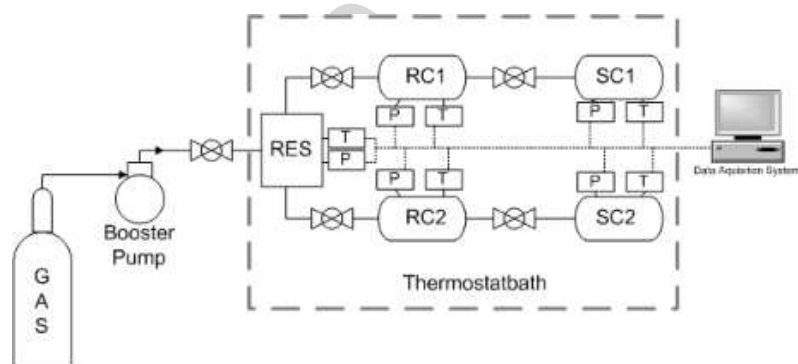


Figure 1: Technical drawing of the manometric set up. RES is the reservoir, RC A is the reference cell A and RC B is the reference cell B, duplicate of A, SC A is the sample cell A and SC B is the sample cell B, duplicate of A, P indicates the pressure transducers and T are the thermocouples.

Table 2: Critical properties and purity of the gases used.

Gas	$T_c$ [K]	$P_c$ [MPa]	$\rho_c$ [mole/m <sup>3</sup> ]	Purity [%]
He	5.1953	0.2274	17399	99.996
N <sub>2</sub>	126.192	3.3958	11183.9	99.9995
CH <sub>4</sub>	190.564	4.5992	10139	99.9995
CO <sub>2</sub>	304.1282	7.3773	10624.9	99.9995

performed simultaneously in part A and part B of the setup. Pressures are measured using the pressure transducers PTX611 manufactured by Drück. Their accuracy is 0.08% FS. The entire setup is immersed in a water-filled thermostatic bath. The temperature is constant within 0.05 K. Experimental temperatures are determined with a PT100 sensor, manufactured by Automated System Laboratories, with an accuracy of 0.02 K. Thermocouples monitor temperature during the experiments to ensure that the temperature is constant. The PTX611 and the K-type thermocouple were connected to a Keithley KPCI-3108 data acquisition and control card connected to a PC with a 16 channel, 16 bits single ended analog input. The valves are controlled with a PC via the data acquisition and control card. Control of the valves is on a time interval basis. The acquisition software is written in Testpoint V3.4. The acquisition software scans the measurements every second and records them every 10 seconds.

### 2.2.2. Swelling measurements

For the swelling experiments strain gauges were glued to the coal blocks in order to reveal the microstrain induced by gas injection. The set up used has been provided by the Department of Mining and Environmental Engineering at Imperial College in London. A full description of the equipment can be found in Durucan et al. (2009).

## 2.3. Experimental procedure

### 2.3.1. Sorption measurements

An experiment for sorption measurements consists of four or five consecutive procedures: (1) He leak rate determination, (2) determination of the volume accessible to gas by a He sorption experiment, (3) actual sorption

and desorption experiment with CO<sub>2</sub>, N<sub>2</sub>, or CH<sub>4</sub>, (4) control measurement of the He sorption and, if necessary, (5) a second leak rate determination.

The leak rate of helium is determined at approximately 20 MPa and at the experimental temperatures of 318 K or 338 K for more than 24 hours. Leakage test are performed until the influence of leakage is determined to be less than 10<sup>-4</sup> mole/kg. At this stage, leakage is not explicitly considered anymore (Hemert et al., 2009). The setup is evacuated at the experimental temperature for 24 hours before the start of the sorption experiment. A sorption experiment consists of two parts: (1) determination of the sorption isotherm and (2) determination of the desorption isotherm. For the sorption isotherm, gas is added step-wise to the evacuated sample cell until a pressure of 14 to 16 MPa is reached. For the desorption isotherm, gas is extracted sequentially from the sample cell until a pressure of 2 to 5 MPa is reached. Table 3 reports the time lag between each step needed to achieve pressure stability.

### 2.3.2. Swelling measurements

For the experimental procedure concerning the swelling experiments a full description of it can be found in the article by Durucan et al.(2009). Swelling has been measured using strain gauges placed on a clean and plane surface of the cubic sample. Measurements have been taken from pure gas (Helium and CO<sub>2</sub>) injections. For each Helium injection an interval of one hour is respected in order to attain equilibrium. For CO<sub>2</sub> a longer time have been respected, between three to six days. Gas is added step-wise to the sample cell until a pressure of 4.1 MPa is reached. The experiment has been performed inside an oven with a constant temperature of 319.4±0.2 K.

## 2.4. Data analysis

### 2.4.1. Sorption measurements

Accurate values of the excess sorption strongly rely on the use of an accurate Equation of State (EoS). In this study, the equation of state for He published by McCarty (1990) is used. For N<sub>2</sub> and CH<sub>4</sub> the equation of state developed by Wagner and Span (1993) is used. For CO<sub>2</sub> the equation of state developed by Span and Wagner (1996) is used. Equations of state give densities  $\rho$  [mol/m<sup>3</sup>] of the gases as a function of pressure  $P$  [MPa] and temperature  $T$  [K]. The excess sorption  $m^N$  [mol/kg] for measurement  $N$  is



Table 3: Experimental conditions and parameters of the sorption experiments.

Exp.	T [K]	$\tau_w$ [h] <sup>1</sup>	M [g]	$\chi$ [-]	$\rho_{\text{coal}}$ [g/mm <sup>3</sup> ]
N <sub>2</sub>	318.20	~ 10	38.44	6.458±0.005	1.65±0.01
			38.59	7.027±0.004	1.85±0.01
	338.06	~ 27	31.51	7.034±0.008	1.68±0.01
			35.05	7.015±0.008	1.67±0.01
CH <sub>4</sub>	318.11	~ 252	35.05	6.995±0.004	1.66±0.01
			31.51	6.979±0.003	1.64±0.01
	338.06	~ 30	35.05	6.995±0.004	1.66±0.01
			31.51	6.979±0.003	1.64±0.01
CO <sub>2</sub>	318.05	~ 72	38.17	3.969±0.028	1.38±0.02
			37.78	4.102±0.012	1.33±0.01
	337.55	~ 72	37.20	4.084±0.002	1.30±0.01

<sup>1</sup> Values reported represent the waiting time respected between each pressure step

obtained from

$$m_{\text{exc}} = \frac{V_{\text{ref}}}{M} \left[ \sum_{i=1}^N (\rho_{\text{fill}}^i - \rho_{\text{eq}}^i) - \chi \rho_{\text{eq}}^N \right], \quad (1)$$

where the the nomenclature is described in Section 6. The volume accessible to gas in the sample cell,  $V_{\text{sc}}[m^3]$  and the reference cell volumes  $V_{\text{ref}}[m^3]$ , are determined using helium expansion. There is no discernible helium sorption effect and it is assumed to be negligible for the determination of  $\chi$ .

$$\chi = \frac{V_{\text{sc}}}{V_{\text{ref}}} = \frac{\rho_{\text{eq}}^i - \rho_{\text{fill}}^i}{\rho_{\text{eq}}^{i-1} - \rho_{\text{eq}}^i}. \quad (2)$$

Equation 2 is adopted for all the measurements; no leakage was detected during the experiments. Table 3 reports all the averaged values of volume ratio obtained in each single experiment including the standard deviation.

#### 2.4.2. Swelling measurements

For the swelling experiments, microstrain are measured using the strain gauges. The coal sample, under hydrostatic gas pressure loading experiences a mechanical deformation in addition to the sorption-induced swelling. The

strain associated to the compression can be estimated using Helium experiments, where no sorption is occurring. The strain can be related to pressure by:

$$\epsilon_p = -c_p P \quad (3)$$

where  $c_p$  [ $MPa^{-1}$ ] is the mechanical compliance coefficient of the sample. The matrix swelling induced by  $CO_2$  injection can then be measured as the net strain between the experimental value and the mechanical compression.

$$\epsilon_m = \epsilon_{exp} - \epsilon_p \quad (4)$$

where  $\epsilon_m$  is the matrix swelling strain and  $\epsilon_{exp}$  is the measured strain.

### 3. Results and discussions

#### 3.1. Equilibration time for the sorption experiments

In total eight sorption experiments were performed. All experiments, except the one with  $CO_2$  were carried out in duplicate. Two sorption experiments have been conducted with  $N_2$  at 318 K and two, always with  $N_2$  at 338 K. In the methane experiments, the temperature for the first two pressure steps was maintained at 318 K. For the following steps the temperature was 338 K. An extra point at 318 K was measured at the last pressure step, before desorption. This procedure was motivated by the long equilibration time needed for  $CH_4$  at 318 K (about ten days). Three experiments were conducted with  $CO_2$ , in the set up with higher accuracy (Hemert et al., 2009); two at 318 K and one at 338 K. According to the experimental measurements the  $CO_2$  experiments equilibration was not fully attained.

Equilibration time for each pressure step is obtained from the pressure versus logarithmic time plot. Therefore, the entire pressure plots (Fig. 2) are discussed. (Clarkson and Bustin, 1999b; Gruskiewicz et al., 2009). Immediately after adding gas to the sample cell, the pressure transducer shows an increase in pressure caused mainly by an "adiabatic" temperature effect. A combination of adiabatic compression in the sample cell and expansion in the reference cell takes place. Temperature equilibration is fast; then the pressure steadily decreases until equilibrium is reached. This has also been observed by other authors. In order to improve legibility of the plots, the first erratic one hundred seconds of the pressure step are eliminated when necessary, therefore the 'adiabatic' effect is not included in the plots.

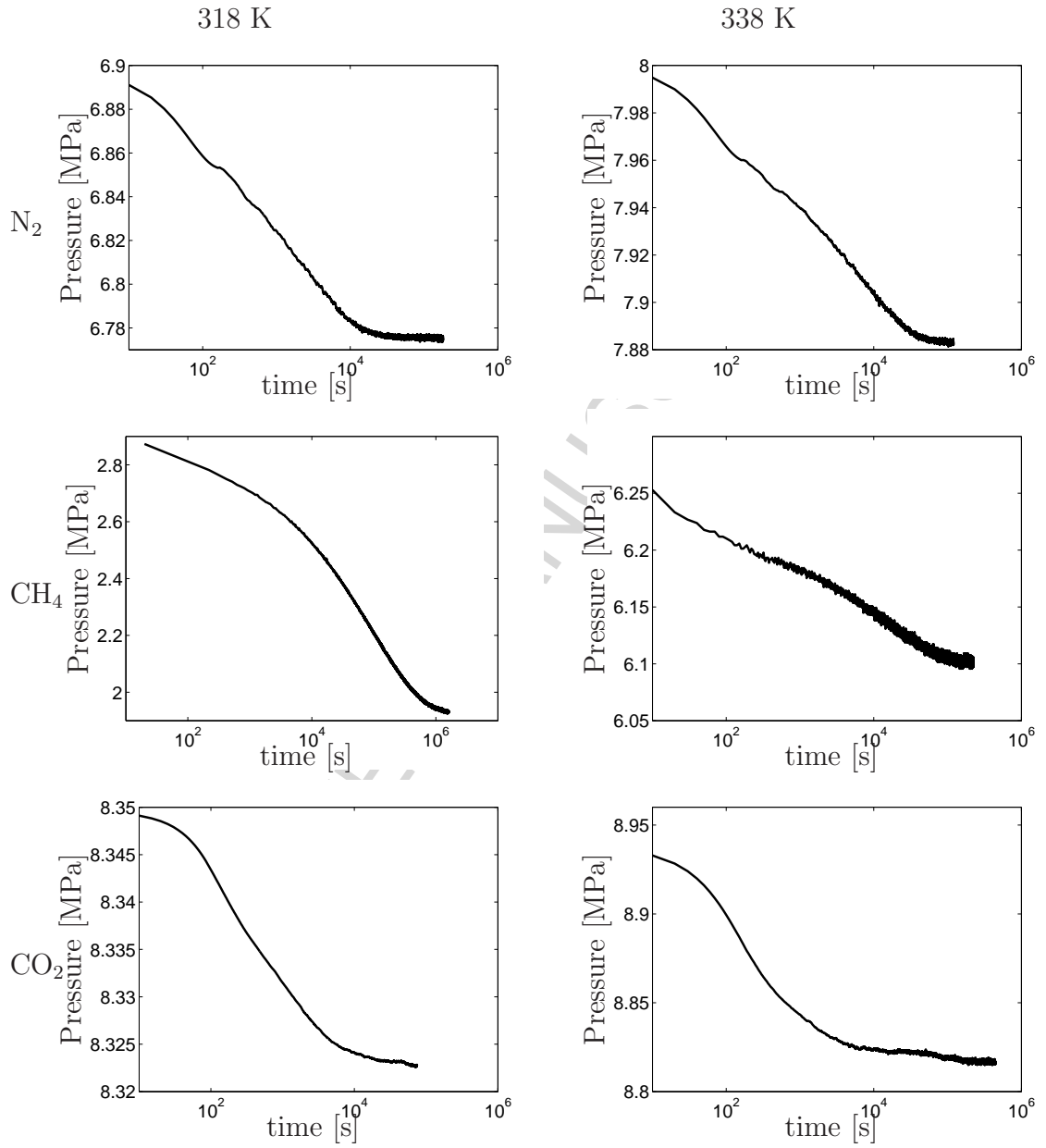


Figure 2: Some examples of pressure decrease steps during sorption of N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> at 318 and 338 K in Selar Cornish coal particles. It is clear that the sorption behavior is different for the different gases and varies with the temperature.

Figs. 2 show the pressure decline history after an adsorption step for  $N_2$ ,  $CH_4$  and  $CO_2$  at 318 K and 338 K. The logarithmic time scale allows a better assessment of the equilibration time, i.e., the time required to attain a constant pressure value. Proper assessment of the equilibration time after every gas injection step is essential because incomplete sorption results in a non-equilibrated excess sorption curve. In figs. 2  $CH_4$  experiment at 318 K shows the largest pressure decrease. This is so because the Langmuir surface is becoming saturated but also, to a lesser extent, because the difference between the gas in its free phase and the gas in the sorbed phase is decreasing. For  $N_2$  and  $CH_4$  equilibration times do not change significantly with pressure, but it does change with gas type and temperature (Table 3). Helium has, at both temperatures, a short equilibration time (one hour) and is not plotted.  $CH_4$  at a temperature of 318 K has an equilibration time of about 10 days as opposed to the much shorter equilibration time at 338 K, i.e., approximately 27 hours. The equilibration time of  $N_2$  shows much less variation, i.e., 10 hours at 318 K and 27 hours at 338 K. Discussion of possible causes for these differences is outside the scope of this paper.

$CO_2$  experiments have been conducted with a fixed interval between each pressure step of 72 hours. Results show that equilibration, after this interval is not fully attained. Equilibration has been checked for a longer time interval for just two pressure steps, during desorption (avoiding the superposition of any possible leak effect on the measurements). Results obtained from these two measurements show that after 2 weeks,  $CO_2$  is still desorbing from coal, at a very low rate.

For the definition of equilibrium, it is very important to consider the set up accuracy and the time scale we are considering. The same results obtained for the  $CO_2$  sorption, if plotted on a linear scale, or measured on a less accurate set up, appear to be equilibrated already after a few hours.

Coal particles with sizes above 0.5 mm are interdispersed with microcleats (Mazumder et al., 2006b) in which diffusion is relatively fast. Therefore, particles above 0.5 mm do not show a large size dependence on equilibration time (Siemons et al., 2003). If coal size particles are below 0.5 mm, the particles between the cleat system are crushed and a much shorter equilibration time is observed as mentioned in other reports (Busch et al., 2004; Siemons et al., 2003; Solano-Acosta et al., 2004).

Our equilibration time are much longer than the one reported in Table 4, apart for Majewska et al. (2009) who was working with coal blocks and Goodman et al. (2006) who plotted pressure decrease versus the squared

Table 4: Literature overview of sorption experiments on different dry coals from other laboratories.

Author	Grain size [ $\mu\text{m}$ ]	Temperature [K]	waiting time [hours]
(Chaback et al., 1996)	93-300	300-320	6-18
(Clarkson and Bustin, 1999a)	1840	273	7
(Busch et al., 2006)	63-2000	318	1
(Goodman et al., 2004)	250	295-328	0.5-12
(Siemons and Busch, 2007)	200	318	20
(Day et al., 2008)	500-1000	326	4
(Gruszkiewicz et al., 2009)	1000-2000	308-313	50
(Majewska et al., 2009)	20000x20000x40000	298	440
(Goodman et al., 2006)	250	328	96
this study	1000-2000	318-338	336

root of time.

The decision of taking big or small grain size needs to be the result of a good compromise between many factors and this will have an important consequence for estimations on a field scale or for obtaining an excess sorption isotherm.

### 3.2. Excess Sorption Isotherm

This section discusses the excess sorption isotherms determined from the mass balance.

Figs. 3, 4 and 5 show the excess sorption isotherm of  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{CO}_2$ .

The  $\text{N}_2$  curve does not show a maximum and the isotherm is monotonically increasing. The maximum error for the duplicate measurements is 0.04 mole/kg at 318 K and 0.07 mole/kg at 338 K. The sorption at  $\approx 5.5 \times 10^3$  mole/ $\text{m}^3$  decreases from  $0.60 \pm 0.02$  mole/kg at 318 K to  $0.53 \pm 0.05$  mole/kg at 338 K. For a single sample the sorption and desorption curves almost coincide.

$\text{CH}_4$  excess sorption isotherm reaches a maximum of 0.92 at 338 K at high pressures, at  $6.2 \times 10^3$  mole/ $\text{m}^3$ . The maximum error of the duplicate measurements is 0.01 mole/kg at 318 K and 0.02 mole/kg at 338 K. The sorption at approximately  $6.2 \times 10^3$  mole/ $\text{m}^3$  decreases from 0.94 mole/kg

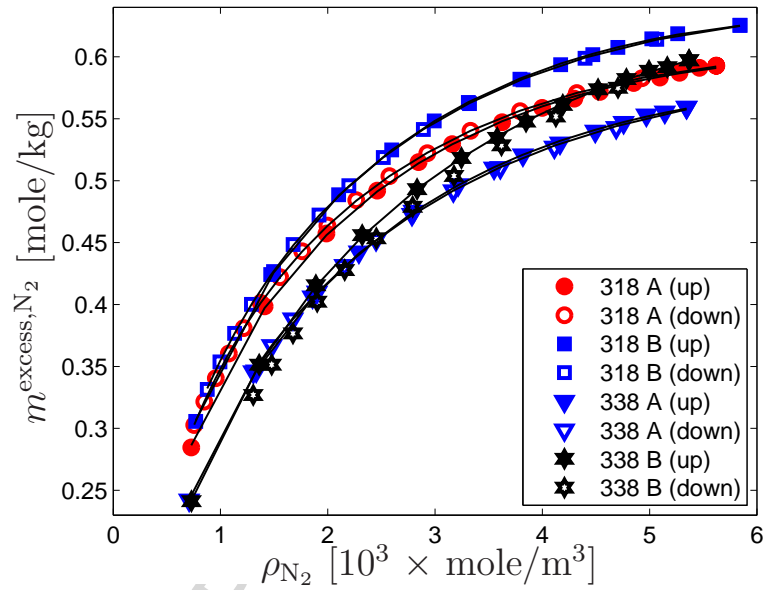


Figure 3:  $N_2$  excess sorption on Selar Cornish coal at 318 K and 338 K. All the curves are fitted using the Langmuir model with two free parameters ( $m_a$ , the saturation capacity of coal and  $b_v$ , the Langmuir equilibrium constant, see Table 5).

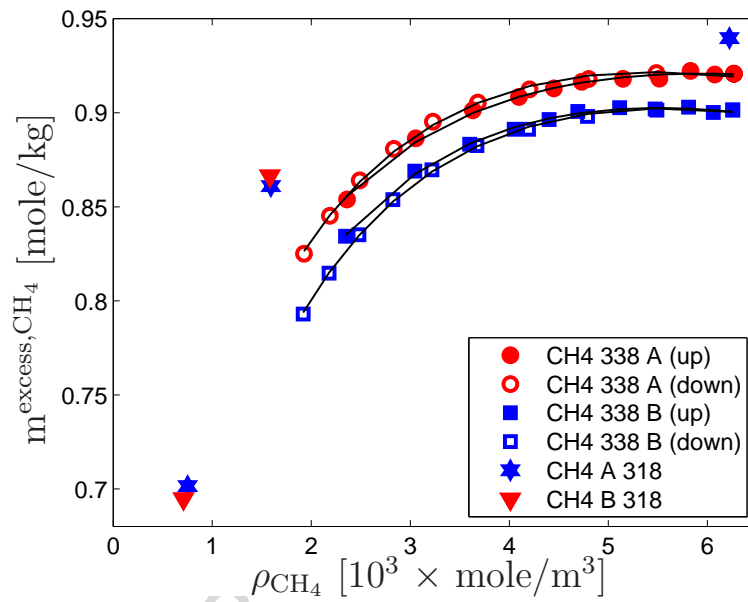


Figure 4: CH<sub>4</sub> excess sorption on Selar Cornish coal at 318 K and 338 K. All curves are fitted using the Langmuir model with two free parameters ( $m_a$ , the saturation capacity of coal and  $b_v$ , the Langmuir equilibrium constant, see Table 5). For the 318 K sorption isotherm only three points have been measured.

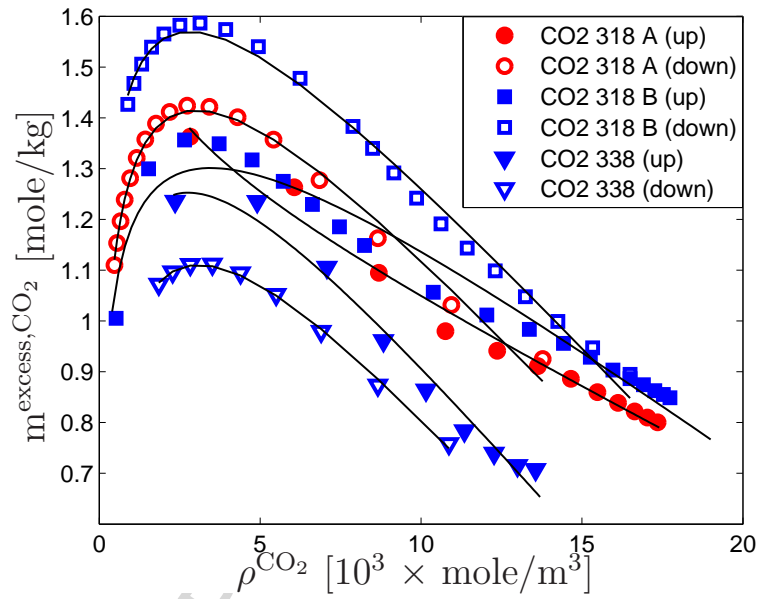


Figure 5: CO<sub>2</sub> excess sorption in Selar Cornish coal at 318 K and 338 K. All the curves are fitted using the Langmuir model with three free parameters ( $m_a$ , the saturation capacity of coal,  $b_v$ , the Langmuir equilibrium constant and  $\rho_a$ , the density of CO<sub>2</sub> in its sorbed phase, see Table 5 ).



at 318 K to  $0.92 \pm 0.01$  mole/kg at 338 K. For a single sample the sorption and desorption curves almost coincide.

Fig. 5 shows the excess (de)sorption of  $\text{CO}_2$  plotted against density of the  $\text{CO}_2$  in its free phase. Plotted versus pressure the isotherms cross over; however, plotted versus density they become linear at high density values. The isotherms show a higher excess sorption value than the one calculated for  $\text{N}_2$  and  $\text{CH}_4$ . The desorption isotherm (338 K) in fig. 5 is lower than the sorption isotherm. The desorption isotherms (338 K) are higher than the sorption isotherms. The error at 318 K is 0.07 mole/kg for sorption data and 0.2 mole/kg or less for desorption data. The error at 338 K could not be determined as only one curve has been measured. When increasing the temperature from 318 K to 338 K the estimated sorption maximum at  $3.5 \times 10^3$  mole/m<sup>3</sup> decreases from  $1.36 \pm 0.03$  mole/kg to 1.24 mole/kg. For the desorption isotherm the variation is much bigger. Note that the "318 A up" intersects with other isotherms, which is considered to be caused by an insufficient number of data points at low pressures.

Isotherms increase up to a maximum around  $3.4\text{-}5.6 \times 10^3$  [mol/m<sup>3</sup>], as reported also by Day et al. (2008) and then decrease linearly. The linearity is the result of the free phase density increase which approaches the density of the adsorbed phase. If it were possible to reach higher pressures in the experiment, the density of the free phase would be equal to the density of the adsorbed phase. Thus, an excess sorption would be zero. In the  $\text{N}_2$  and  $\text{CH}_4$  excess sorption this apparent decrease in the sorption is not visible because the gas density in the free phase is much lower than the gas density of the sorbed phase.

$\text{CO}_2$  measurements cannot represent an equilibrated excess sorption isotherm. None of the data point in the fig.5 represent a situation where equilibrium has been attained. Reason to this limitation have been explained in the previous section (see Section 3). Measurements on  $\text{CO}_2$  are in agreement with the recent literature data (Ottiger et al., 2008; Sakurovs et al., 2007). The grain size distribution is not influencing the excess sorption isotherm but just the equilibration time (Siemons et al., 2003).

The ratios between the maximum in the excess sorption are  $\text{N}_2:\text{CH}_4:\text{CO}_2 = 1:1.5:2.6$  at 318 K and  $1:1.5:2.0$  at 338 K. This is within the range mentioned in the literature (Busch et al., 2003). The temperature dependance of the  $\text{N}_2$  equilibrium sorption is lower than for  $\text{CO}_2$  and  $\text{CH}_4$ .

The hypothesis that sorption on coal is reversible, given appropriate waiting time at each pressure step, is confirmed in the experiment with  $\text{N}_2$  and

CH<sub>4</sub>. There are several reasons that may cause the apparent hysteresis in the CO<sub>2</sub> sorption.

- The sample have been dried following a specific procedure (see Section 2 ) but the remaining moisture content in the coal sample actually is not known. The water in the sample is dispersed creating chemical bonds with coal surface. Even a small amount of water then can affect CO<sub>2</sub> sorption kinetics and sorption processes.
- Another reason that can explain the apparent hysteresis might be the insufficient waiting time. In view of the extremely long equilibration times, the reversibility of CO<sub>2</sub> sorption in coal is still an open question.
- The absorption process creates chemical interactions between coal and CO<sub>2</sub> molecules that can be not fully reversible (van Bergen, 2009).

The reversibility of the sorption process is a new observation but results are in agreement with existing literature on activated carbon (Dreisbach et al., 1999; Salem et al., 1998; Sebastian and Jasra, 2005) and with the reversibility of the swelling and shrinkage process caused by the CO<sub>2</sub> sorption and desorption on coal (see section 3.3).

In this study the Langmuir (L) isotherm model has been chosen in order to fit our data. The Langmuir equation is based on the concept of an equilibrium between the gas molecules in the sorbed state at a sorption site and gas molecules in the free gas phase. In order to maintain the linearity in the CO<sub>2</sub> excess sorption isotherm and to lead to a closer connection to the fugacity term, the Langmuir equation was adapted (Sakurovs et al., 2007):

$$m_{\text{exc}} = \frac{m_a \rho_g}{b_v + \rho_g} \left( 1 - \frac{\rho_g^{\text{e}}}{\rho_a} \right), \quad (5)$$

where  $m_{\text{exc}}$  is the excess sorption,  $m_a$  is the saturation capacity per unit mass of coal,  $b_v$  is the Langmuir equilibrium constant,  $\rho_a$  is the adsorbed phase density of the gas and  $\rho_g$  is the density of the gas in the free phase. The bracketed term converts to excess sorption (Mavor et al., 2004).

Figs. 3, 4 and 5 show the fitted Langmuir isotherms as drawn lines.

For CH<sub>4</sub> and N<sub>2</sub>, Eq.5 have been used with two free parameters:  $m_a$  and  $b_v$ . The densities of the sorbed phase are assumed equal to the densities of the liquid phase:  $25.02 \times 10^3 \text{ mol/m}^3$  and  $22.04 \times 10^3 \text{ mol/m}^3$ , respectively for N<sub>2</sub> and CH<sub>4</sub> (Sudibandriyo et al., 2003). The resulting averaged parameters are

presented in Table 5. The Langmuir isotherm show excellent agreement with the experimental data . The sum of the squared difference of the sorption data with respect to the fitted curve is always equal or less than 0.01.

For the carbon dioxide data the two parameter fit is not adequate to represent the excess sorption isotherm. This is so because the gas phase density of carbon dioxide in our experiment starts to approach the density of the sorbed phase. Therefore, the density of the sorbed phase has been kept as a fitting parameter. Results of the fitted parameters are displayed in Table 5. In the literature there is a large variety of densities used (Siemons and Busch, 2007). In the experiments described in this paper, the fitted density of the sorbed phase is varying between  $21.86 \times 10^3 \text{ mol/m}^3$  and  $44.01 \times 10^3 \text{ mol/m}^3$ . The density of the gas in its sorbed phase obtained with the model fitting have been compared with the one extrapolated from the excess sorption isotherm, following the methodology described by Sudibandriyo (Sudibandriyo et al., 2003). Values obtained are in good agreement with the models results. The density of  $\text{CO}_2$  in its sorbed phase measured on activated carbon gives much smaller values, e.g.  $22.72 \times 10^3 \text{ mol/m}^3$  (Hemert et al., 2009). The increase in the density of the  $\text{CO}_2$  in its adsorbed phase during sorption on coal can be attributed to specific dissolution processes on the coal matrix when  $\text{CO}_2$  is in its supercritical phase (Huang et al., 2005).

### 3.3. Swelling measurements

Free swelling has been measured on two different cubic samples of Selar Cornish coal. The strain gauges on one sample are placed over a plane surface and on the other sample are placed on two normal plane surfaces. In total three different linear strains have been measured. Fig.6 shows the volumetric swelling (in percentage) of the two different samples of Selar Cornish coal induced by  $\text{CO}_2$  injection, at a constant temperature of  $321 \pm 0.2 \text{ K}$ . The swelling in the two plane is almost the same, which means that the swelling is isotropic for this coal. The volumetric strain is three times the the linear strain. The data show that swelling is a fully reversible process, as already noticed by other laboratories (Chikatamarla et al., 2004; Day et al., 2007). Free swelling is proportional to the volume of gas sorbed and the amount of gas on coal is related to the density by a Langmuir equation. Thus also the swelling effect can be described by a Lanmguir type curve (Levine, 1996), see Fig.6. Experimental results have been fitted with a Langmuir type curve .

$$\epsilon_v = \frac{\epsilon_{\max} \rho_g}{b_V + \rho_g}, \quad (6)$$

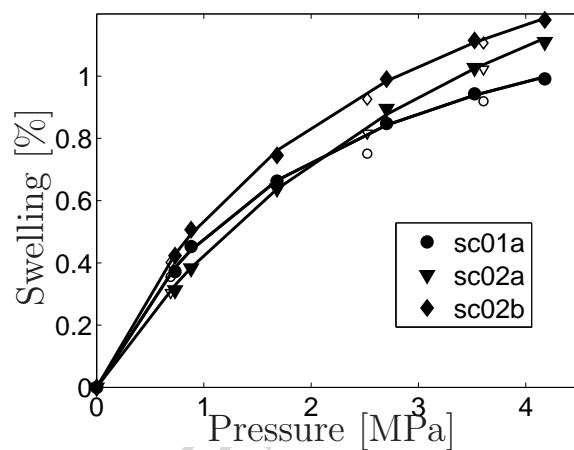


Figure 6: Volumetric swelling induced by  $\text{CO}_2$  sorption on two different samples of Selar Cornish coal (sc01 and sc02) at  $321 \pm 0.2$  K. Letters a and b in the legend indicate that the calculated swelling is obtained from measurements on two different planes of the same cubic sample. The unfilled symbols represent shrinkage induced by desorption. Experimental results have been fitted with a Langmuir isotherm. Parameters values are reported in Table 5.

where  $\epsilon_v$  is the volumetric swelling,  $\epsilon_{\max}$  is the maximum volumetric swelling and  $b_v$  is the Langmuir constant.

### 3.4. Absolute sorption isotherm

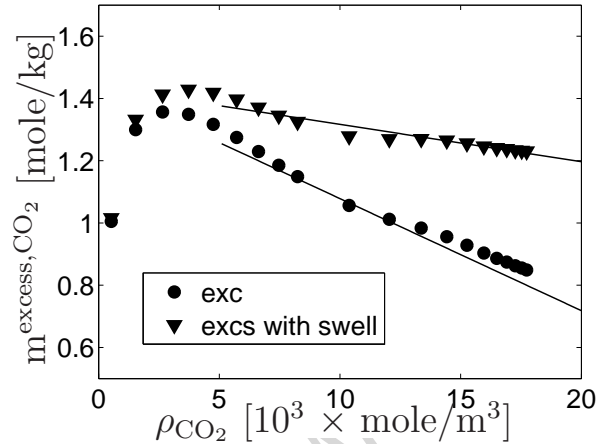


Figure 7: Excess sorption isotherm of  $\text{CO}_2$  on Selar Cornish coal at 318K. The circles represent the excess sorption considering a constant sample cell volume the triangles are estimated considering also the change in volume due to the swelling of coal during  $\text{CO}_2$  sorption .

For ECBM application the absolute sorption isotherm as well as the excess sorption are of interest. The absolute sorption is the total amount of gas residing in the coal per unit mass, it is taking in account also the gas in its sorbed phase; this leads to a decrease of the volume accessible to the gas because sorption sites are occupied by the gas after every injection. At low pressure the gas has a substantially lower specific density than the one in the adsorbed phase and the volume of the latter can be neglected. At higher pressure values, the density of the gas in its supercritical phase is of the same order of magnitude of the density of the sorbed phase. The measurements are affected by the non-ideality of the gas phase and the volumetric effects of the condensed phases (coal swelling, increase of the sorbed phase volume, etc.) are no longer negligible.

The transformation methods from excess sorption to absolute sorption either use constants  $\rho_a$  (density of the gas in the sorbed phase) or constant

$V_a$  (volume of the gas in the sorbed phase)(Murata et al., 2001). Some authors prefer to develop the isotherm curve from assuming a constant  $V_a$  (Ottiger et al., 2006) and some as in this paper assume  $\rho_a$  constant. This leads to the following equation(Mavor et al., 2004):

$$m_{exc} = m_{abs} \left( 1 - \frac{\rho_g}{\rho_a} \right) \quad (7)$$

The above absolute sorption isotherm takes into account the gas in its sorbed phase but it ignores any swelling effect. The absolute sorption isotherm has been rewritten incorporating coal volume changes due to the CO<sub>2</sub> absorption

$$m_{abs} = n_T - \rho_g[V_{sc} - (\rho_a m_a) - (V_0(\epsilon_v + 1))], \quad (8)$$

where  $n-T$  is the total amount of CO<sub>2</sub> in moles and  $V_0$  is the initial volume of the unswollen coal. parameters derivation is included in the Appendix.

In Fig.7 plots of the excess sorption are compared. One has been calculated assuming a constant volume accessible to the gas in the free phase and the other one assuming a volume reduction due to swelling. The sorbed density values have been calculated as described in section 3.2. For the case of a constant volume accessible to the gas, the extrapolated value is  $\rho_a=42.06 \times 10^3 \text{ mol/m}^3$ . For the case of a volume reduction due to swelling, the extrapolated value is  $\rho_a=114.03 \times 10^3 \text{ mol/m}^3$  The extrapolated value obtained for the case of a volume reduction due to swelling is unrealistic if it is interpreted as the sorbed density of the CO<sub>2</sub>. Possible reasons for this high values are:

- CO<sub>2</sub> is also affecting the coal structure (absorption)
- It has been assumed that the swollen coal has the same porosity as the unswollen coal,  $\phi=0.03$  (Mazumder, 2007)

Fig.8 presents the two absolute sorption isotherms, one considering just the effect of the volume occupied by the gas in its sorbed phase and the other one including also the effect induced by the swelling of the coal. Using excess sorption data and Eq.7 and using excess sorption data with Eq.8 leads to the same sorption isotherm. This similarity is the result of the mathematical procedure.

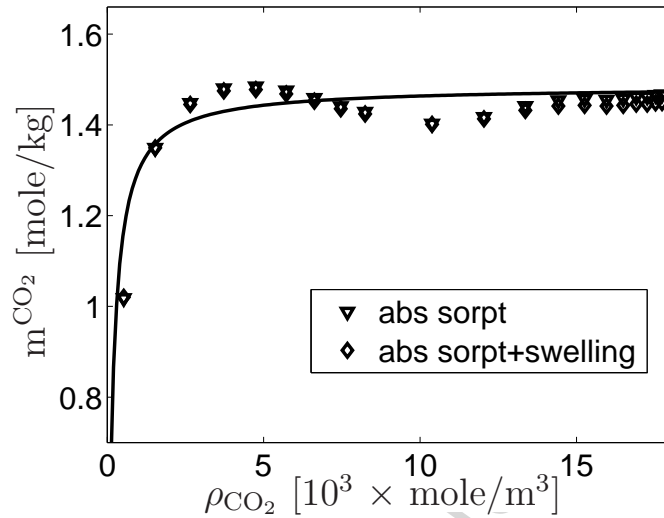


Figure 8: Absolute sorption of  $\text{CO}_2$  on Selar Cornish coal at 318 K. The triangles represent the absolute sorption curve and the diamonds represent the absolute sorption curve including also the swelling effect. The Langmuir equation is fitted to the absolute sorption isotherm(continuous line), the parameters are displayed in Table 5 .

#### 4. summary of observations

For the experiments with Selar Cornish coal the following observations are made:

- Experimental results indicate that the time required for attaining sorption equilibrium for  $\text{N}_2$  is 10 h at 318 K and 27 h at 338 K; for  $\text{CH}_4$  it is 10 days at 318 K and 30 hours at 338 K; for  $\text{CO}_2$  it exceeds 72 h at 318 K and 338 K. It has been proved by the experiments that the time required for equilibration varies with the type of gas, temperature. Thus, results are in line with the expectation that during flue gas injection methane is produced first and subsequently nitrogen will reach the production well while carbon dioxide lags behind. In the field case, methane desorbs first as a consequence of its in situ presence and pressure drop near the production well.
- The excess sorption isotherm of nitrogen monotonically increases to a

maximum of  $0.60 \pm 0.02$  mole/kg at 318 K and  $0.53 \pm 0.05$  mole/kg at 338 K. The excess isotherm of  $N_2$  shows no hysteresis.

- The excess sorption of methane monotonically increases to a plateau of  $0.92 \pm 0.01$  mole/kg at 318 K and  $0.94 \pm 0.01$  mole/kg at 338 K. The excess isotherm of  $CH_4$  shows no hysteresis.
- The excess sorption of carbon dioxide increases with increasing gas density up to a density of approximately  $4 \times 10^3$  mole/ $m^3$  with a maximum of  $1.36 \pm 0.03$  mole/kg at 318 K and a maximum of 1.24 mole/kg at 338 K. After the maximum is reached, the excess sorption decreases strongly with increasing density. This behavior is in agreement with recent gravimetric measurements in the literature for  $CO_2$  sorption in coal. The excess isotherm of  $CO_2$  shows hysteresis. Whether this is due to insufficient waiting times after each pressure step and or other phenomenon is still an open question.
- Swelling measurements on unconfined cubic samples reveal that  $CO_2$  sorption induces a swelling effect on coal. The phenomenon is fully reversible. Data are fitted with a Langmuir isotherm. Langmuir parameters are: a maximum swelling of  $\epsilon_{max} = 1.42 \pm 0.17$  % and a Langmuir constant of  $b_v = 1.38 \pm 0.33$  MPa.
- The absolute sorption for  $CO_2$  has been calculated in two different ways. First no correction for swelling was made and the density of the sorbed phase extrapolated from the excess sorption was used in order to obtain the absolute sorption isotherm. In the second case, swelling correction was used and again the extrapolated density of the sorbed phase was used in a correction factor to convert the excess sorption isotherm to the absolute sorption isotherm. The two absolute sorption isotherm are almost the same. However, the extrapolated density for the swelling corrected case is unrealistically high. The absolute sorption isotherm curve has been fitted with a Langmuir type of curve. The saturation capacity per unit mass of coal is  $m_a = 1.8$  mole/Kg and the Langmuir equilibrium constant is  $b_v = 3.9 \times 10^3$  mol/ $m^3$ .

## 5. Conclusions



Table 5: Langmuir parameters of the different isotherm fitting.  $\rho_a$  is the density of the gas in its sorbed phase,  $b_v$  is the Langmuir equilibrium constant and  $m_a$  is the saturation capacity per unit mass of coal. The parameters calculated for the absolute sorption are not presented with an error analysis because they were calculated over a single experiment

	N <sub>2</sub> <sup>1</sup>	CH <sub>4</sub> <sup>1</sup>	CO <sub>2,exc</sub>	CO <sub>2,abs</sub>	swelling <sup>2</sup>
$\rho_a$ [ $\times 10^3$ mol/m <sup>3</sup> ]	25.02	22.04	21.86-44.01	42.06	-
$b_v$ [ $\times 10^3$ mol/m <sup>3</sup> ]	1.33 $\pm$ 0.32	0.34 $\pm$ 0.05	0.37 $\pm$ 0.11	1.8	1.38 $\pm$ 0.17
$m_a$ [mol/Kg]	0.73 $\pm$ 0.04	0.97 $\pm$ 0.01	1.63 $\pm$ 0.18	3.9	1.38 $\pm$ 0.33

<sup>1</sup> the density of the gas in the adsorbed phase has been taken from literature (Sudibandriyo et al., 2003)

<sup>2</sup> the second parameter of the swelling is not the total mass sorbed but the maximum swelling ( $\epsilon_{max}$ , [%])

Equilibrium in each of the pressure step can be established after that there is no noticeable change in pressure. To assess it correctly it is necessary to plot the pressure in a logarithmic time scale. This can be accomplished for N<sub>2</sub> and CH<sub>4</sub>. The equilibrium cannot be accomplished for CO<sub>2</sub> due to extremely long experimentation time. For N<sub>2</sub> and CH<sub>4</sub> the excess sorption isotherm does not show any hysteresis. CO<sub>2</sub> excess sorption isotherm do show hysteresis. One of the causes can be ascribed to the insufficient waiting time. Other cause can be the residual water content in the coal sample. Even a small amount of water can affect CO<sub>2</sub> sorption kinetics and sorption processes. Other reason can be ascribed to the fact that during absorption the gas seems to react with the coal molecules creating bonds that could be not fully reversible.

All the excess sorption and desorption isotherms and the swelling/shrinkage measurements can be fitted using a Langmuir curve. The physical meaning of the extrapolated absolute density of CO<sub>2</sub> obtained from the excess sorption isotherm is not clear. This can indicate that either the line extrapolation is not a valid method or the model of adsorbate storage is oversimplified. Other factors, besides coal swelling and the volume of the adsorbed phase, could affect excess sorption isotherm. Excess sorption data may not provide enough information to accurately determine all unknowns and explain

molecular-scale phenomena.

The free swelling results show that coal swelling accounts for most of the decline in the CO<sub>2</sub> excess sorption at high pressures.

## 6. Acknowledgement

The experiments have been performed under the GRASP (Green-House Gas Removal Apprenticeship) programme. We are really thankful to the department of Mining and Environmental Engineering at Imperial College of London and particularly to Sevket Durucan for allowing the internship and Shafiuddin Amer Syed for all the laboratory work concerning the swelling experiments. Experiments of gas sorption on coal have been performed at Dietz Laboratories of TUDelft, we are really thankful to Henk Van Hasten for his technical help.

## 7. Appendix

The absolute sorption is the total amount of fluid residing per unit mass. In the sorption experiments it can be described as

$$m_{abs} = n_T - \rho_g V_g, \quad (9)$$

where  $V_g$  is the volume of the gas in the sample cell in the free phase,  $\rho_g$  is the density of the CO<sub>2</sub> its free phase,  $n_T$  is the total amount of CO<sub>2</sub> present in the sample cell,  $m_{abs}$  is the absolute amount of CO<sub>2</sub> adsorbed per mass of coal and  $m_{exc}$  is the excess amount of CO<sub>2</sub> adsorbed per mass of coal. The volume of the sample cell ( $V_{sc}$ ) is assumed to be constant and can be expressed as

$$V_{sc} = V_g + V_{coal} + V_a, \quad (10)$$

where  $V_a$  is the volume occupied by the CO<sub>2</sub> in the sorbed state and  $V_{coal}$  is the volume occupied by the coal sample. The volume occupied by the CO<sub>2</sub> in the sorbed state can be defined as

$$V_a = \frac{m_{abs}}{\rho_a}, \quad (11)$$

where  $\rho_a$  is the density of the gas in the sorbed phase and it is assumed to be constant. The coal is swelling due to the CO<sub>2</sub> sorption. The volume of coal can be expressed as

$$V_{coal} = V_0(\epsilon_v + 1), \quad (12)$$

where  $V_0$  is the initial volume of coal,  $\epsilon_v$  is the volumetric swelling that can be obtained using the Langmuir isotherm:

$$\epsilon_v = \frac{\epsilon_{\max}\rho_g}{b_V + \rho_g}, \quad (13)$$

where  $\epsilon_{\max}$  is the maximum swelling and  $b_v$  is the Langmuir constant. The absolute sorption can be calculated including also the swelling effect in it. Substituting Eq.10, Eq.11 and Eq.12 in Eq.9, we obtain:

$$m_{abs} = n_T - \rho_g[V_{sc} - (\rho_a m_a) - (V_0(\epsilon_v + 1))]. \quad (14)$$

The unknown of the system are:  $m_{abs}$ ,  $V_a$ ,  $V_g$  and  $V_{coal}$ . The value of the density of the gas in its adsorbed phase has been extrapolated from the excess sorption curve and compared with the model results on the excess sorption fitting (see 3.4), the  $b_V$  and  $\epsilon_{max}$  parameter of the Langmuir fitting have been taken from the experimental results. The system of equations has been solved using the Solver of Excel.

Table 6: Nomenclature

<i>Symbol</i>	<i>Unit</i>	<i>Physical quantity</i>
$m_{exc}$	[mole/kg]	(Gibbs) Excess sorption
$m_{abs}$	[mole/kg]	Absolute sorption of gas
$n_t$	[mol/kg]	Total amount of gas present in the sample cell per mass of coal
$M$	[kg]	Coal mass after evacuation
$P$	[MPa]	Pressure
$\rho_{fill}^i$	[mole/m <sup>3</sup> ]	Molar density of gas at the i-th filling step
$\rho_{eq}^i$	[mole/m <sup>3</sup> ]	Molar density of gas at the i-th equilibrium step
$\rho_a$	[mole/m <sup>3</sup> ]	Molar density of gas in the adsorbed phase
$\rho_g$	[mole/m <sup>3</sup> ]	Molar density of gas in the free phase
$\chi$	[-]	Volume ratio of sample cell to reference cell
$V_{sc}$	[m <sup>3</sup> ]	Volume accessible to the gas in the sample cell
$V_{ref}$	[m <sup>3</sup> ]	Volume of the reference cell
$V_g$	[m <sup>3</sup> ]	Volume of the gas in the sample cell in the free phase
$V_a$	[m <sup>3</sup> ]	Volume of the gas in the adsorbed phase
$V_{coal}$	[m <sup>3</sup> ]	Volume of the coal
$V_0$	[m <sup>3</sup> ]	Initial volume of the coal
$c_p$	[MPa <sup>-1</sup> ]	Mechanical compliance effect
$\epsilon_p$	[-]	Measured strain
$\epsilon_{exp}$	[-]	Matrix swelling strain
$\epsilon_v$	[%]	Volumetric strain
$\epsilon_{max}$	[%]	Maximum volumetric strain
$m_a$	[m <sup>3</sup> /kg]	saturation capacity per unit mass of coal
$b_v$	[mol/m <sup>3</sup> ]	Langmuir equilibrium constant

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