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European inter-laboratory comparison of high pressure CO_2 sorption isotherms. I: Activated carbon

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ABSTRACT

In order to assess and improve the quality of high-pressure sorption isotherms of carbon dioxide (CO_2) on coals, an inter-laboratory study ("Round Robin") has been conducted among four European research laboratories. In a first round of measurements, excess sorption isotherms were determined on Filtrasorb 400 (F400) activated carbon at 318 K using the manometric (TU Delft and RWTH Aachen University) and the gravimetric (FP Mons and INERIS) method up to 16 MPa. The study shows that CO_2 sorption in the supercritical range can be determined accurately with both gravimetric and manometric equipment but requires thorough optimization of instrumentation and measuring as well as proper sample preparation procedures. For the characterization of the activated carbon F400, which we used as benchmark, we have determined a surface area of $1063 \, m^2 \, g^{-1}$, and Dubinin-Radushkevich (DR) micropore volume of $0.51 \, cm^3 \, g^{-1}$. Additionally, we analysed the elementary near-surface composition by energy dispersive X-ray spectroscopy (EDX). To characterise the bulk composition of the F400 activated carbon, a proximate and ultimate analysis was performed.

The observed excess sorption maxima around 5 MPa have values around $8.0 \, mol \, kg^{-1}$, which are consistently higher (by upto $0.8 \, mol \, kg^{-1}$) than literature data.

1. Introduction

Among the various options considered for geological storage of carbon dioxide (CO_2), the injection of CO_2 into deep, unminable coal seams in particular in combination with the production of coalbed methane (CBM), is considered a niche technology. The European RECOPOL[1] project has demonstrated the technical feasibility of CO_2 injection into typical European Carboniferous coal seams. The follow-up project MOVECBM[2] started in 2006 to investigate in more detail the fate of injected CO_2. Laboratory experiments conducted by the two groups at the Delft University of Technology (The

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  [1] http://recopol.nitg.tno.nl/.
  [2] http://www.movecbm.eu.

Notation

$K_{L,V}$	Langmuir parameter (MPa)		T	temperature (K)
$m_{transferred}$	mass transferred from reference to sample cell (g)		t_{equil}	time taken for equilibration (h)
			s_{excess}	excess sorption (mmol g^{-1})
m_{coal}, m_{sample}	mass of activated carbon or coal (g)		$s_{absolute}$	absolute sorption (mmol g^{-1})
m_{excess}	excess sorption mass (g)		V_R, V_{ref}	reference cell volume (cm^3)
Δm	incremental sample weight in gravimetric experiment (g)		V_V, V_{void}	void volume of sample cell (cm^3)
			V_{sample}	skeletal volume (cm^3)
n	amount of substance of gas (mmol)		z_{ri}	initial reference real gas compressibility factor
p	Gas pressure (MPa)		z_{rf}	final reference real gas compressibility factor
p_i	i = equil. p in sample cell of previous sorption step, i + 1 = equil. pressure of filling the reference cell, i + 2 = equil. pressure in sample cell of sorption step (MPa)		z_{si}	initial sample real gas compressibility factor
			z_{sf}	final sample real gas compressibility factor
			σ_i	inaccuracy of measurement of parameter i
			ρ^{i,CO_2}	free phase density of CO_2 in reference cell at time-step i (before connecting with sample cell), e = equilibrium density (after connecting with sample cell) (g cm^{-3})
p_{ri}	initial reference cell pressure (MPa)			
p_{rf}	final reference cell pressure (MPa)			
p_{si}	initial sample cell pressure (MPa)			
p_{sf}	final sample cell pressure (MPa)		ρ_{sample}	skeletal density of the sample (g cm^{-3})
$R = 8.31451$	gas constant (J mol^{-1} K^{-1})			

Netherlands) within the Dutch CATO[3] project and RWTH Aachen University (Germany) within RECOPOL[1] and the national CO2TRAP[4] project provided important fundamental information on the interaction of natural coals with carbon dioxide and methane under in-situ conditions.

However, considerable problems in the reproducibility of supercritical CO_2 sorption measurements became evident. Similar problems were encountered by other groups and have been addressed by two recent inter-laboratory studies [1,2]. The results of these studies showed that, in spite of considerable improvements in accuracy, the quality of CO_2 sorption isotherms does not yet meet the standards required for reliable modeling and predictions [22].

In this context the four laboratory research groups at Delft University of Technology (TU Delft), RWTH Aachen University (RWTH), INERIS and Faculté Polytechnique Mons Belgium (FP Mons) decided to perform an inter-laboratory study to assess and improve the quality of sorption data at high pressures for supercritical carbon dioxide. In contrast to earlier inter-laboratory tests [1,2] this study was set up as an open project with exchange of information and regular seminars. The main objective was to increase the overall accuracy of CO_2 excess sorption measurements, eliminate pitfalls and sources of error and develop best practice standards and procedures.

A well-characterized activated carbon sample, Filtrasorb 400 (F400), was selected for the first series of measurements. This material is homogeneous, readily available and its chemical composition and micropore structure are similar to those of natural coal. Furthermore, F400 is resistant to high temperatures. This facilitates the removal of moisture and attainment of a defined initial condition, one of the main sources of discrepancies in earlier inter-laboratory comparisons. The F400 has been used in pervious CO_2-sorption studies [3–6] so that published reference data were available for comparison.

Sorption experiments were performed at 318 K up to 16 MPa. These are typical conditions for coalbeds suitable for CO_2 storage with pressures ranging from 6 to 15 MPa and temperatures between 300 and 330 K.

The most common procedures to determine excess sorption isotherms of gases are the manometric [9–12] and the gravimetric method. [4,5,15,16,24,25] These are well established and known to provide accurate excess sorption isotherms for simple and well-characterized sorption systems (e.g. methane sorption on activated carbon). Both methods were used in this study.

1.1. Previous inter-laboratory comparisons of carbon dioxide sorption on coal at high pressures

Two inter-laboratory comparison studies on high-pressure sorption of CO_2 on Argonne Premium coals [1,2] were initiated by the US Department of Energy-National Energy Technology Laboratory (DOE-NETL). Although experienced research groups were involved in these inter-laboratory tests, large deviations were observed. The discrepancies were attributed to varying moisture contents. Goodman et al. concluded that further studies with well-defined procedures are required to improve reproducibility. Therefore, in the present study, time and temperature for evacuation have been increased to ensure complete removal of remnant moisture.

The first inter-laboratory study [1] compared the sorption isotherms of CO_2 on dry coals at 295 and 328 K up to a pressure of 7 MPa measured by five laboratories. Five types of coal, covering a maturity range from 0.25% to 1.68% vitrinite reflectance, were used. The preparation procedure involved drying of the samples for 36 h at 353 K under vacuum. It was found that excess sorption values for medium- to low-rank coals deviated by more than 100%. Sorption isotherms on high-rank

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coals were considered to be sufficiently accurate. The discrepancies were attributed to varying residual moisture contents after drying of the coal samples.

The second inter-laboratory study [2] compared the sorption isotherms of CO_2 on moisture-equilibrated coals at 328 K and pressures up to 15 MPa measured by six laboratories. Moisture-equilibration was achieved by a modified ASTM D 1412-99 procedure [7]. Three types of coal, covering a maturity range from lignite to high volatile bituminous, were used. Sorption data showed good agreement for pressures up to 8 MPa. However, at higher pressures sorption diverged significantly for the different laboratories. This deviation was attributed to substantial variations in moisture contents.

2. Methods and materials

2.1. Sample and sample preparation

FILTRASORB® 400 (F 400) activated carbon of Calgon Carbon Corporation used in this study was kindly supplied by Chemviron Carbon GmbH, Germany. Aliquots of the same batch (Batch No.:FE 05707A) were distributed among the participants in order to ensure identical sample properties. Analytical data for the F400 have been previously published by Fitzgerald et al. [3].

The pore size characterization of the F400 batch used in this study was determined by a low pressure nitrogen adsorption isotherm at 77 K (80 data points, from 7×10^{-6} to 0.9965 p/p_0 (Fig. 1a), evaluated using the nonlocal density functional theory (NLDFT). Additionally, the pore diameter distribution over the complete range and an enlargement of the range between 0 and 5 nm are shown in (Fig. 1b and c). The prominent peaks are at 0.8 and 1.2 nm. The BET specific surface area is 1063 m^2/g, calculated over 10 data points in the relative pressure range between 0.1 and 0.3. The Dubinin–Radushkevich (DR) micropore volume is 0.51 cm^3/g, determined in the relative pressure range between 4×10^{-5} and 3×10^{-2} over 28 data points (Table 6). Nearly the same pore-size distribution (PSD) was determined on a different batch of AC F400 by Jagiello and Thommes [8] using N_2 and Argon as sorbents. All measurements in the present study were performed on dry sample material. The activated carbon was dried at 473 K for 24 h (see below for description of the drying procedures).

2.2. Sample preparation

The drying procedures differed slightly among the participating laboratories. In three laboratories the sample was dried in the measuring cell to avoid any contact with atmospheric air after drying.

At RWTH Aachen the sample (5–7 g) was degassed at 473 K in the sample cell used for sorption measurements. The sample cell was placed into a heating sleeve and heated to 473 K under vacuum (10^{-2} Pa) for 24 h.
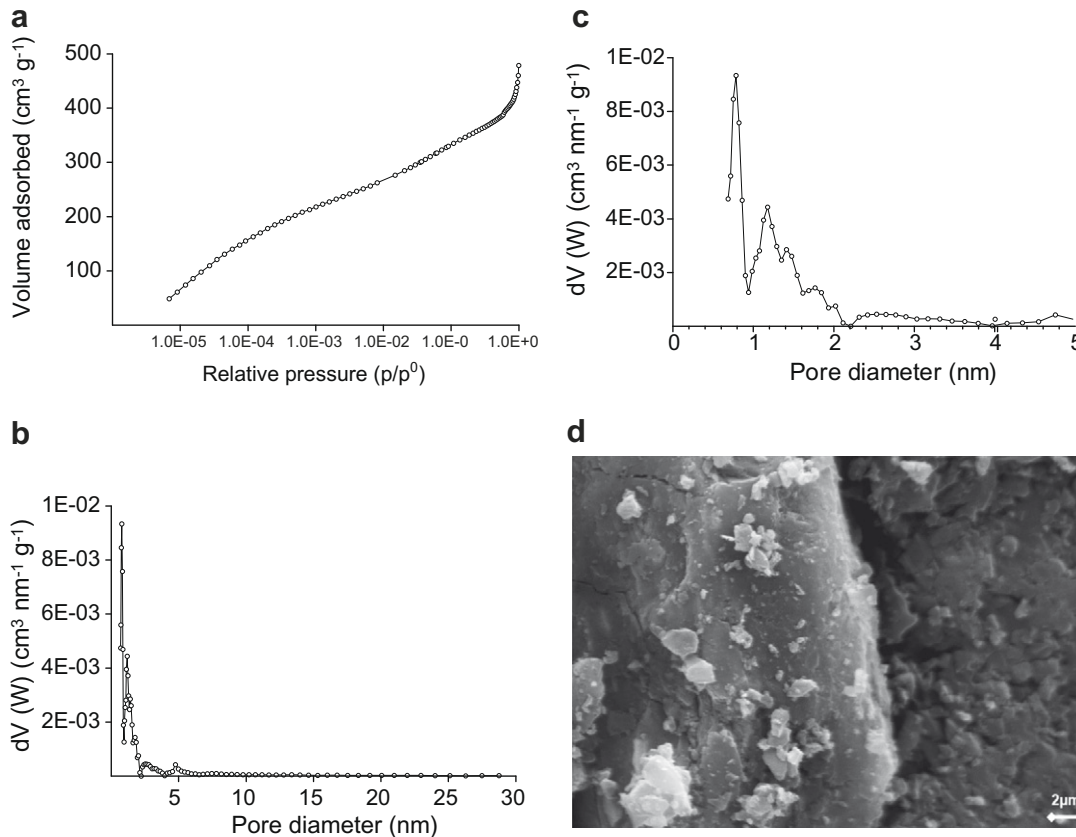
Fig. 1 – (a) N_2 isotherm at 77 K (80 data points, 7×10^{-6} to 0.9965 p/p_0) for the F400 activated carbon sample in a log plot. (b) Pore diameter distribution over the complete range based on NLDFT and (c) enlarged view of the range between 0 and 5 nm. (d) SEM picture including EDX-Analysis (see Table 1).

At FP Mons, about 1.5–2 g of original sample were degassed for 24 h at 10^{-2} Pa using a turbomolecular pump with a temperature ramp of 1 K min^{-1} up to 473 K.

At the TU Delft laboratory the sample cell containing ∼35 g of sample was detached from the sorption set-up, placed in an electric oven and heated under vacuum to 473 K for 24 h. The evacuation pressure of the pump was <100 Pa. To avoid air influx, the sample cell was filled with He before transfer to the sorption set-up.

At INERIS about 1.5–2 g of original sample was dried in an oven at 473 K for 24 h. Afterwards it was placed into the sample cell, which was then evacuated to 10^{-1} Pa for another 24 h before the start of the experiment.

2.3. Experimental methods

Three different techniques are commonly used to determine gas sorption isotherms on coals: the *manometric* [9–12] or *piezometric* [13] method, the *volumetric* method [14] and the *gravimetric* method [5,15,16]. Modern gravimetric sorption devices mostly employ magnetic suspension balances that allow contactless weighing of samples across the walls of closed high-pressure systems. The principles of the different techniques are discussed by Goodman et al. [1,2]. Although these three methods make use of different physical principles and parameters, they usually provide accurate and comparable sorption isotherms for simple and well-characterized sorption systems (e.g. methane on activated carbon or natural coals). The primary experimental parameter obtained from all these procedures is the excess sorption (Gibbs sorption, Gibbs excess) [13] (see Tables 4 and 5).

2.4. Manometric set-up (RWTH Aachen, TU Delft)

Sorption experiments at RWTH Aachen University and TU Delft were performed using the manometric technique with customized in-house experimental devices (see Table 3 for details). Both set-ups have the same basic components such as reference volume, measuring cell, valves, high-precision pressure gauges and temperature control units, but differ in size.

In the manometric or piezometric procedure, defined amounts of gas are successively transferred from a calibrated reference cell into the measuring cell containing the coal sample. Prior to the sorption experiment the void volume of the measuring cell (V_{void}^0) is determined by expansion of a "non-adsorbing" gas – typically helium – using Boyle's law

and the McCarthy He-EoS. [26] This procedure also provides the skeletal volume (V_{sample}^0) and the skeletal density (ρ_{sample}^0) of the sample. The void volume, multiplied by the density of the gas (or supercritical phase ($V_{void}^0 \cdot \rho^{CO_2}(T,p)$), yields the "non-sorption" reference mass, i.e. the amount of gas (supercritical fluid) that would be accommodated in the measuring cell if no sorption took place. The excess sorption mass ($m_{excess}^{CO_2}$) is the difference between the mass of gas that has been actually transferred into the measuring cell up to a given pressure step, and the "non-sorption" reference mass:

$$m_{excess}^{CO_2} = m_{transferred}^{CO_2} - V_{void}^0 \cdot \rho^{CO_2}(T,p) \tag{1}$$

The mass transferred from the reference cell into the measuring cell during N successive pressure steps is given by:

$$m_{transferred}^{CO_2} = \sum_{i=1}^{N} V_{ref} \cdot \left(\rho_i^{f,CO_2} - \rho_i^{e,CO_2} \right) \tag{2}$$

Here the superscripts f, CO_2 and e, CO_2 refer to the density of CO_2 in the reference cell before it is connected with the sample cell and after equilibration, respectively.

The excess sorption mass is usually normalized to the initial mass of the sorbent. In the present study it is expressed in units of amount of substance (mol/kg or mmol/g).

2.5. RWTH Aachen University

The manometric units at RWTH Aachen University have been described previously by Krooss et al. [9] and Busch et al. [10]. They are equipped with Tecsis Series P3382 pressure sensors with internal diaphragm. Pressure ranges are from primary vacuum (10^{-2} Pa rotary vane vacuum pump) up to 16 or 25 MPa with an accuracy of ±0.05% of the full-scale (FS) value and standard output is an RS 232-interface.

Two pneumatically actuated Valco 3-port switching valves with 1/16" connectors are used to control the gas transfer through the calibrated reference volume and into the sample cell. The reference volume consists of the void volume of the pressure sensor and the 1/16" stainless-steel tubing between the switching valves. The reference volume is in the range of 1.7 cm^3 and is determined by helium expansion with an accuracy of ±0.0003 cm^3.

The entire manometric set-up (valves, pressure sensor, measuring cell) is kept in a thermostated air bath. Thermostatic ovens of different suppliers (Heraeus, Binder, Varian) are in use for the various sorption set-up presently operated in the RWTH laboratory.

Table 1 – EDX elemental analysis averaged over the total surface (Fig. 1d).

Atom%	C	O	Al	Si
EDX (this study)	85 ± 1	11.5 ± 1	1.5 ± 0.5	2 ± 0.5

Table 2 – F400 Proximate and ultimate analysis parameters.

%	C	O	N	S	H	Moisture	Fixed carbon	Vol. matter	Ash
This study	89.55 ± 0.22	5.77 ± 0	0.25 ± 0.04	0.77 ± 0.01	0.21 ± 0.02	1.52 ± 0.17	91.06 ± 0.28	1.32 ± 0.03	6.10 ± 0.11
Fitzgerald[3]	88.65	3.01	0.4	0.73	0.74	–/–	89.86	3.68	6.46

Table 3 – Specifications of experimental devices used in this inter-laboratory study.				
Method	RWTH Aachen Manometric	TU Delft Manometric	FP Mons Gravimetric	INERIS Gravimetric
Max. CO_2 pressure (MPa)	25 ± 0.0125	20.7 ± 0.001	16 ± 0.016	5 ± 0.01
Measuring temperature (K)	318.6 ± 0.2 318.8 ± 0.2	318.11 ± 0.02 318.12 ± 0.02	318.5 ± 0.1 318.6 ± 0.1	318.2 ± 0.1
Sample mass (g)	5–7 ± 0.0001	34.95 ± 0.03 35.57 ± 0.03	1.69804 ± 0.00002 1.68711 ± 0.00002	2.0151 ± 0.0002
Sample cell volume (cm^3)	13.085 ± 0.001	78.33 ± 0.06 75.9 ± 1	–	–
Reference cell volume (cm^3)	1.7785 ± 0.0003	12.152 ± 0.009 3.524 ± 0.004	–	–
Average void volume (cm^3)	10.450	61.1 ± 0.1 59.2 ± 0.1	–	111.5 ± 0.2
Volume of the system (crucible + sample) (cm^3)	–	–	1.575 ± 0.002 1.684 ± 0.002	1.68 ± 0.01
Equilibration time (h)	1–2	303	1–3	24
CO_2 purity	99.995%	99.990%	99.996%	99.998%

The experimental temperatures were monitored using type K (NiCr–Ni) thermocouples (Roessel Messtechnik GmbH,) connected to a Keithley Model 2000 Multimeter equipped with a 2001-TCSCAN Thermocouple Scanner Card with cold junction compensation (CJC). Reference measurements with a high-precision (class A) Pt100 Resistive Temperature Detector (RTD) revealed that the temperature readings taken via the thermocouples were consistently lower than the true temperatures. The offset ranged from 0.1 up to 0.4 °C. The *a priori* uncertainty of the excess sorption measurements, determined by a blank isotherm is in the order of 0.005 mmol. Further specifications of the experimental set-up are listed in Table 3.

2.6.   TU Delft

The volumes of the TU Delft sorption set-up and the sample amounts used in the measurements are approximately six times larger than those used at RWTH Aachen. It is equipped with a 9000 series Paroscientific pressure sensor with a piezo-electric element. The entire set-up is immersed in a thermostated water bath (Lauda RP485) that keeps temperature variations within 0.03 K. Temperature is measured with a Pt100 RTD with an accuracy of 0.02 K and recorded by an F200 reader (Automated System Laboratories). The cells are connected by pneumatically actuated 2-position Valco valves. The main contributions to the *a priori* uncertainty of 0.04 mmol/g are discussed by van Hemert et al. [17].

2.7.   Gravimetric method (FP Mons, INERIS)

In the gravimetric instruments the sorbent is placed into the high-pressure compartment of a magnetic suspension balance (Rubotherm) and exposed to the sorptive, CO_2, at constant temperature and increasing pressure. The excess sorption is determined from the mass change of the sample ($\Delta m = m_{measured}\ (T, p) - m_{sample}^0$) recorded during this procedure, where m_{sample}^0 is the original sample mass. This apparent sample mass change is corrected by a buoyancy term based on the skeletal volume (V_{sample}^0) of the sample, i.e., the same reference state as in the manometric procedure. The determination of the skeletal density or volume is performed with helium, which is assumed to be non-adsorbing.[18] The excess sorbed mass is then given by:

$$m_{excess}^{CO_2} = \Delta m + V_{sample}^0\ \cdot \rho_{CO_2}\ (T, p) \tag{3}$$

$$m_{excess}^{CO_2} = \Delta m + \frac{m_{sample}^0}{\rho_{sample}^0}\ \cdot \rho_{CO_2}\ (T, p) \tag{4}$$

As in the manometric procedure, it is normalized to the original sample mass m_{sample}^0 and expressed in molar units (mol/kg) in this study.

The FP Mons set-up is discussed in detail by De Weireld et al. [19,20]. The most important technical features are as follows:

The weight changes are measured with a 10 µg accurate Rubotherm magnetic suspension balance. The magnetic system consists of an electromagnet linked to the balance and a permanent magnet at the top of the suspension system for the crucible containing the sorbent. The suspension system is housed in a high-pressure adsorption chamber allowing for experiments under high temperature (243–393 K), high pressure (vacuum- to 15 MPa) and corrosive conditions. Pressure is measured with three different pressure sensors, an MKS Baratron 621B with a resolution of 1.3 Pa for secondary vacuum to 133.3 kPa, an MKS Baratron 621B with a range from 32.5 Pa for secondary vacuum up to 3.333 MPa and a Tecsis Series P3382 pressure sensor with internal diaphragma for a maximum pressure of 16 MPa with an accuracy of 0.1% of the full scale. Temperature measurements of the gas phase for the determination of the density are performed with a high-precision (class A) Pt100 RTD. The installation is placed in a thermostatic oven ensuring constant temperature during experiments. This homogeneous temperature field avoids condensation of sub-critical gases [24,25]. The *a priori* uncertainty of the excess sorption measurements is estimated at 5% of the maximum sorption.

The INERIS apparatus is very similar to the FP Mons set-up. At INERIS the pressure was measured with one pressure sensor (GE Sensing PMP4010) with an accuracy of 0.08% of the full scale value. Temperature measurements of the gas phase for the determination of the density were performed with a Pt100

RTD from Thermosensor GmbH with an accuracy of ±0.05 K. The *a priori* uncertainty of the excess sorption measurements is estimated at 5% of the maximum sorption.

3. Results

The 318 K sorption isotherms for CO_2 measured on the F 400 activated carbon measured by the participating groups are plotted in Fig. 2 on a linear (a) and a logarithmic pressure axis (b). These plots of excess sorption vs. pressure show an increase until a maximum value of ~8 mmol/g is reached at a pressure of ~5 MPa. Subsequently, excess sorption decreases with an inflection point around 10 MPa.

Table 4 lists the maximum excess sorption values of the individual experiments and the respective measuring temperature. The helium skeletal density values of the F400 activated carbon measured in these tests (Table 4, column 4) are essentially identical.

Duplicate measurements of the excess sorption isotherms within the individual laboratories show excellent intra-labo-

ratory repeatability with deviations of 0.4%, 0.3%, 0.2% for RWTH Aachen, FP Mons and TU Delft respectively.

The inter-laboratory comparison shows that the RWTH Aachen excess sorption values are slightly higher than those of the other participants in the 1–8 MPa pressure range with a maximum deviation of ~0.3 mmol/g. In the high pressure range from 12 to 16 MPa the excess sorption data of FP Mons are somewhat (~0.3 mmol/g) lower than those of the two other laboratories. Generally, the level of accuracy for these types of experiments is good to excellent and the variability in the sorption data of the different laboratories is considered acceptable.

In Fig. 3 the excess sorption values of the laboratories FP Mons, TU Delft and RWTH Aachen are plotted versus the density of the free CO_2 phase at the corresponding pressure and temperature conditions. These isotherm plots exhibit the typical shape discussed by Menon [21]. Maximum excess sorption values of approximately 8 mmol/g are reached by all isotherms at a CO_2 density around 100 kg/m³. Beyond a CO_2 density of ~250 kg/m³ the excess sorption isotherms decrease
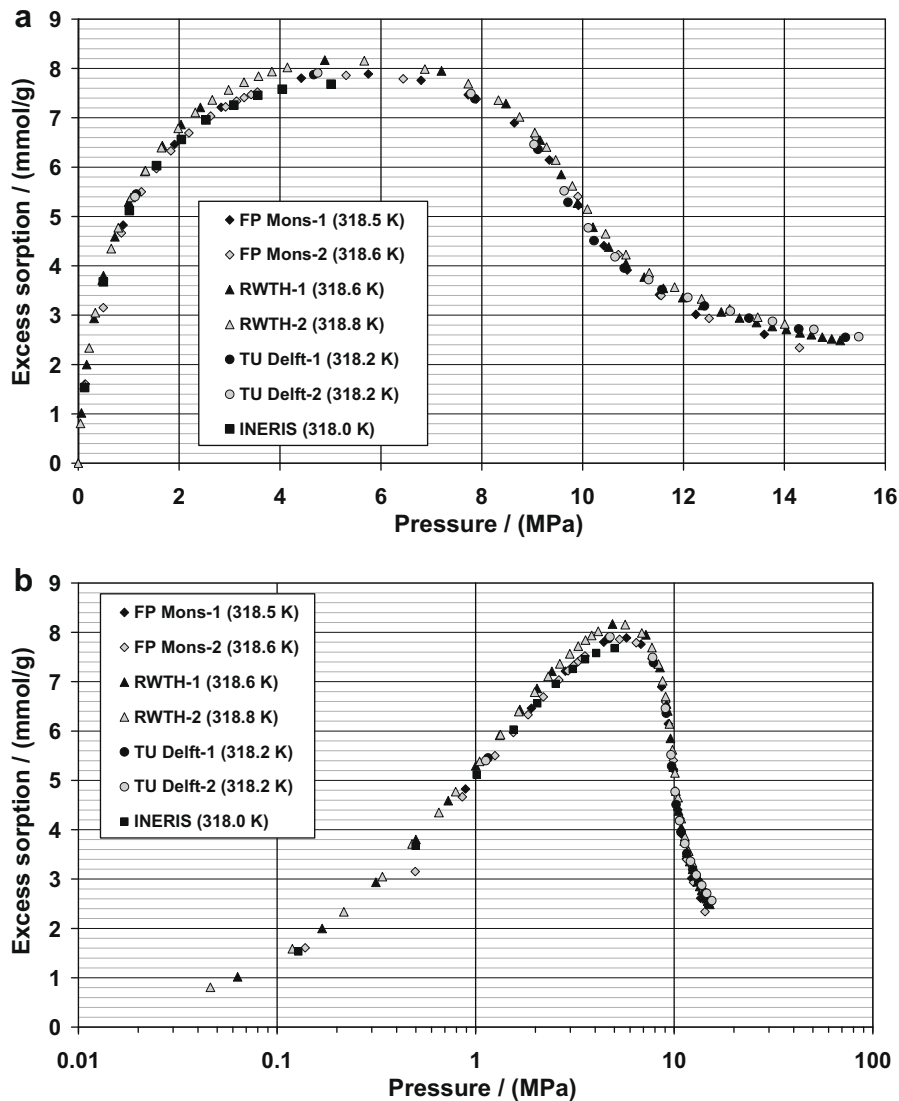

Fig. 2 – Excess CO_2 sorption isotherms on activated carbon Filtrasorb F400 plotted on a linear (a) and a logarithmic (b) pressure axis.

Table 4 – Comparison of experimental results for CO_2 excess sorption isotherms on F400 activated carbon.

	n_{max} (mmol/g)	T (K)	Skeletal density (kg/m^3)
FP Mons-1	7.95	318.5	2140
FP Mons-2	7.87	318.6	2200
RWTH-1	8.23	318.6	2110
RWTH-2	8.17	318.8	2113
TU Delft-1	7.97	318.2	2070
TU Delft-2	7.99	318.2	2100
INERIS	7.67	318.2	2280
Average	8.0		2140
Std. dev.	0.16		70
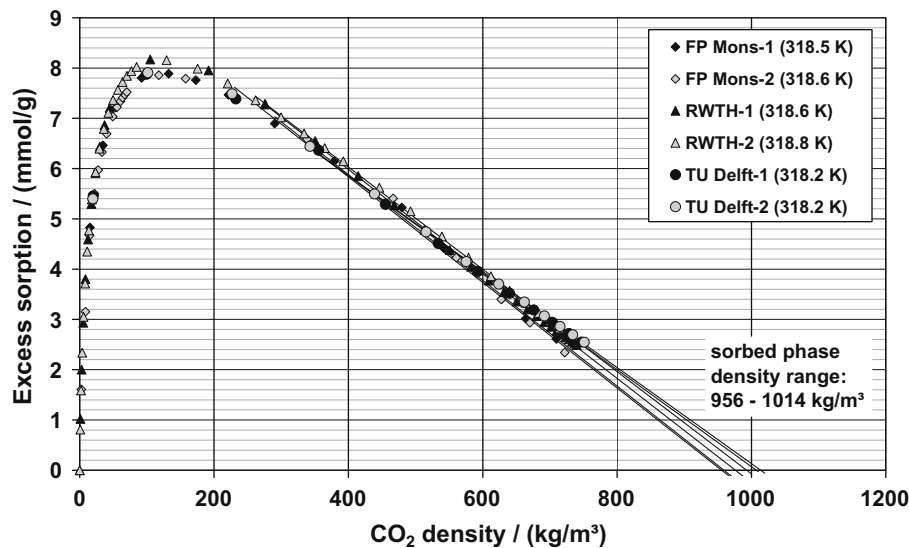
Fig. 3 – Excess sorption versus density of free gas phase (using the Span and Wagner equation) [23] for activated carbon Filtrasorb F400 at 318 K.

linearly. The intercept of the extrapolated linear trend with the density axis provides an estimate of the density of the sorbed phase (see Fig. 3). At this point the densities of the free phase and the adsorbed phase are identical, i.e. the two phases cannot be discriminated any longer. The density of the adsorbed CO_2 was estimated by extrapolation of the excess sorption *vs.* density plots in the density range >250 kg/m^3. The density values obtained by this procedure ranged from 956 to 1014 kg/m^3. The lowest density values arose from the FP Mons data while the highest values were obtained from the TU Delft results.

3.1. Parameterization of the experimental results

The experimental high-pressure CO_2 excess sorption isotherms obtained in this study were approximated by the following excess sorption function:

$$s_{excess}\ (T, p) = s_{absolute}\ (T, p) \cdot \left(1 - \frac{\rho_{free}\ (T, p)}{\rho_{sorbed}}\right)\ [\text{mmol/g}] \qquad (6a)$$

Here the absolute amount of adsorbed substance, $s_{absolute}\ (T, p)$, was expressed by the Langmuir function:

$$s_{absolute}\ (T, p) = s_{absolute}^{\infty} \cdot \frac{p}{K_{L,V} + p} \qquad (6b)$$

This function was chosen because it is a simple, steady function increasing monotonously with pressure, that can be derived from the concept of a dynamic equilibrium between free and adsorbed molecules. The Langmuir parameters $K_{L,V}$ and $s_{absolute}^{\infty}$ and the density of the adsorbed phase (ρ_{sorbed}) in Eq. (6) were adjusted simultaneously by a least-square regression. The Langmuir coefficient $K_{L,V}$ is the controlling factor of the absolute (6b) and, in consequence, of the excess sorption function (6a) in the low-pressure region where the volume of the adsorbed phase is negligible. The density ratio $\left(\frac{\rho_{free}\ (T, p)}{\rho_{sorbed}}\right)$ of the free ("gas") vs. the sorbed gas phase controls the shape of the isotherm above the critical pressure when the density of the free, supercritical CO_2 phase increases rapidly.

The results of the regressions for the individual experimental excess sorption isotherms are listed in Table 5. The quality of the fits is expressed by the parameter Δn according to Eq. (7). Here N is the number of data points of the isotherm, and n and n_{fit} are the measured and the fitted excess sorption values of data point n.

$$\Delta n = \frac{1}{N} \sqrt{\sum_{1}^{N} (n - n_{fit})^2} \qquad (7)$$

Table 5 – Regression parameters of CO$_2$ excess sorption isotherms on F400 activated carbon obtained as best 3-parameter fits of Eq. (6) to experimental results of this study. The density of the sorbed phase could not be determined from the INERIS isotherm because the isotherm was only measured up to 5 MPa.

|	$s_{absolute}^{\infty}$ (mmol g^{-1})	$K_{L,V}$ (MPa)	ρ_{sorbed} (kg m^3)	Δn (quality of fit)
FP Mons-1	11.19	1.235	963	0.030
FP Mons-2	11.03	1.225	964	0.036
RWTH-1	11.1	1.036	976	0.033
RWTH-2	11.2	1.099	993	0.030
TU Delft-1	11.0	1.126	992	0.013
TU Delft-2	10.99	1.283	995	0.010
INERIS	(10.0)	(0.90)	(981)	0.042
Average	11.09	1.167	981	
Std. dev.	0.085	0.087	13.5	
Tel. std. dev.	0.8%	7.4%	1.4%	
Best fit for all experimental data of this study:				
EU-Round Robin	10.97	1.082	997	0.019

Also listed in Table 5 (bottom line) is the parameter set that provided the best fit of Eq. (2) to the seven excess sorption isotherms measured by TU Delft, FP Mons, INERIS and RWTH Aachen during this inter-laboratory study. Prior to this regression calculation the data densities of the experimental curves were homogenized in order to avoid a bias that might result from different data densities of individual isotherms in certain pressure intervals. Fig. 4 shows the experimental sorption isotherms with the regression function based on the best fit parameters in Table 5.

In Fig. 5 the normalized deviations ($s_{regression} - s_{measured}$)/$s_{regression}$) of the experimental data from the best fit function are plotted vs. pressure. It is evident from this diagram that the majority of experimental data points in the pressure range >1 MPa fall within ±5% of the regression function. This relative deviation is of the same order as the overall variability of the experimental data from the participating laboratories. Thus, the Langmuir-based regression function can be considered to represent, at present, with sufficient accuracy high-

pressure CO$_2$ excess sorption isotherms measured in different laboratories.

3.2. Comparison with previously published results

Fig. 6 shows a set of previously published CO$_2$ isotherms for F400 activated carbon (Humayun and Tomasko [4], Pini et al. [5], Sudibandriyo et al. [6]). Also included in this diagram is the best fit excess sorption isotherm obtained in the present inter-laboratory study. The locations of the excess sorption maxima and the extrapolated sorbed phase densities (cf. Humayun and Tomasko [4]) coincide with those obtained in the present study, but the maximum excess sorption values of the present set of experiments are consistently higher by approximately 10%. This slightly higher excess sorption capacity is most probably due to differences in sample preparation or due to difference in the sample batch. While the activation temperature in this study was 200 °C over 24 h, Humayun and Tomasko [4] dried the sample at 110 °C over
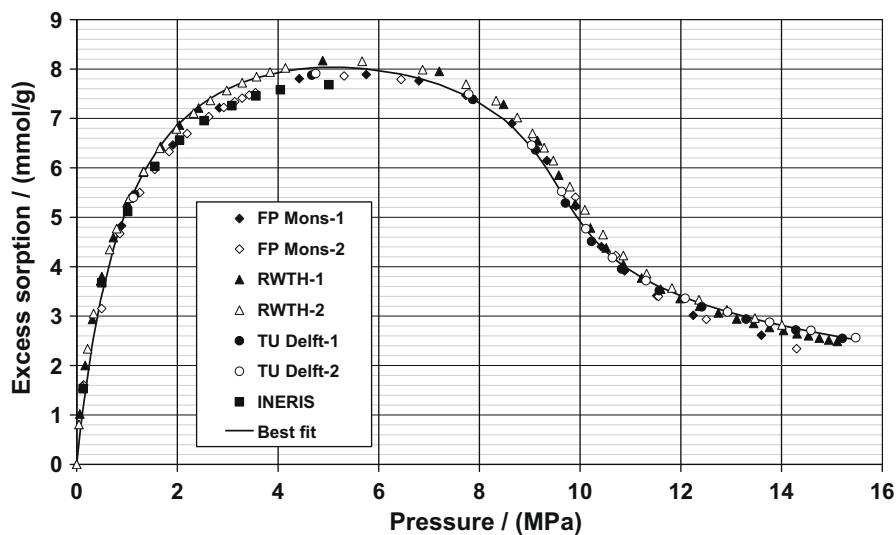
Fig. 4 – Experimental excess sorption isotherms (318 K) for Filtrasorb F400 activated carbon measured in this study with best fit of excess sorption function according to Eq. (6).
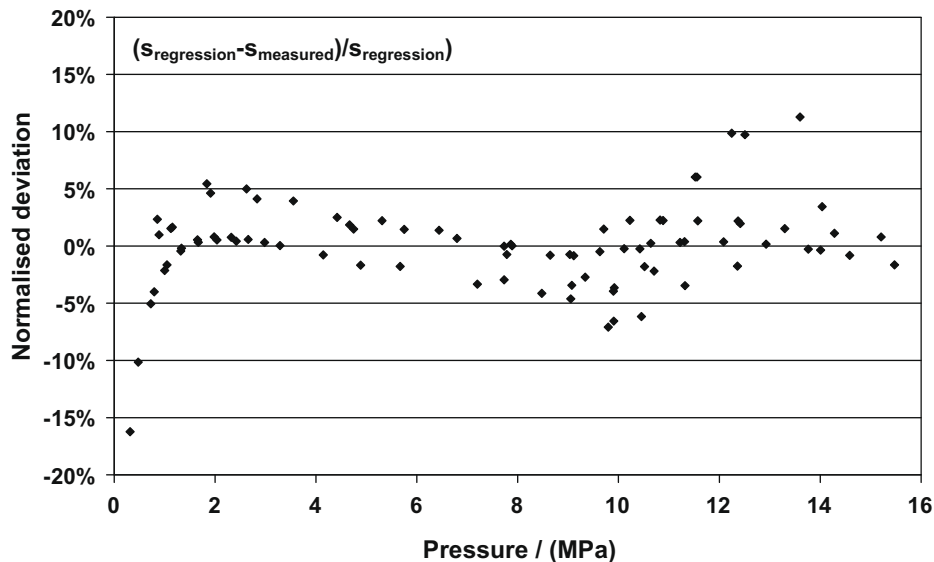
Fig. 5 – Normalized deviation of all experimental CO_2 excess sorption isotherms (318 K) for F400 determined in this study from the best fit vs. pressure.
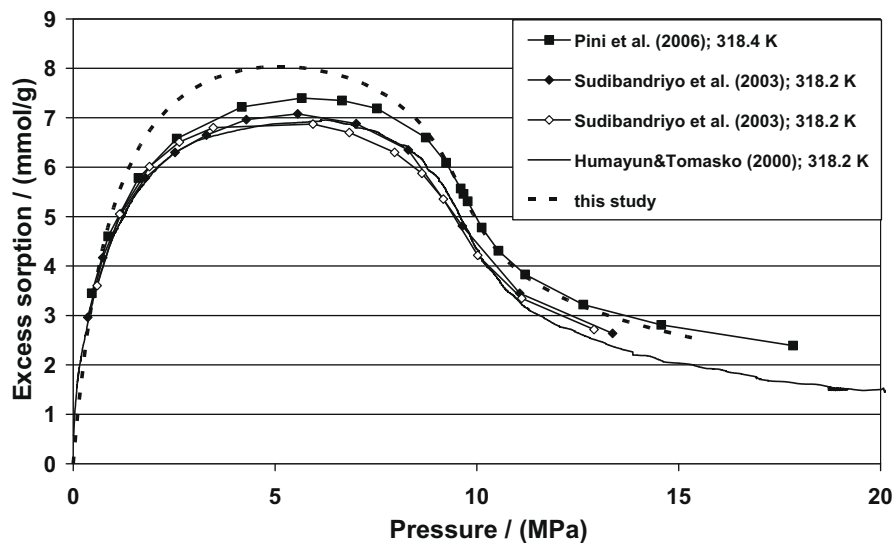

Fig. 6 – Comparison of CO_2 excess sorption results for F400 activated carbon of the present study (dashed line) with literature data.

12 h. Furthermore, the procedure of the EU round robin explicitly required either *in-situ* activation of the F400 samples or transfer to the measuring cell without exposure to air. Humayun and Tomasko [4] report for their F400 batch a BET specific surface area of 850 $m^2 g^{-1}$ and a micropore volume of 0.37 $cm^3 g^{-1}$ determined by N_2 sorption at 77 K. The batch used in our study had a BET surface area of 1063 $m^2 g^{-1}$ (determined at RWTH Aachen by N_2 sorption at 77 K at over 10 data points in the relative range between 0.1 and 0.3). The DR micropore volume of our batch was 0.51 $cm^3 g^{-1}$, determined in the relative pressure range between 4×10^{-5} and 3×10^{-2} over 28 data points (Table 6).

Table 6 – characteristic surface parameters determined from low-pressure N_2 isotherm at 77 K.			
	BET surface area ($m^2 g^{-1}$)	DR Micropore volume ($cm^3 g^{-1}$)	NLDFT Micropore volume ($cm^3 g^{-1}$)
F400 batch of this study	1063	0.51	0.64
Humayun and Tomasko [4]	850	0.37	–/–

3.3. Discussion

The inter-laboratory studies on CO_2 sorption on natural (Argonne Premium) coals by Goodman et al. [1,2] have revealed substantial discrepancies among the results of the participating laboratories. The European inter-laboratory study on high-pressure CO_2 sorption, initiated in a joint attempt to overcome these experimental problems, has yielded very promising results. The isotherms determined by the participating laboratories on an F400 activated carbon sample showed an excellent agreement with inter-laboratory deviations <5% and a very good intra-laboratory reproducibility (variations <1%). Workshops and exchange of technical information among the member groups during the first phase of this initiative have substantially contributed to an improvement of sample preparation and measuring procedures and the identification of potential errors and pitfalls in the determination of high-pressure CO_2 sorption isotherms. The direct comparison of manometric and gravimetric techniques indicated excellent agreement. Selected issues concerning the accuracy of the experimental measurements are discussed briefly in the following sections and the appendix.

3.4. Effect of moisture content and variability of batch composition

To study the effects of even short-term exposure to atmospheric air/moisture, one set of sorption measurements was performed at RWTH Aachen with F400 aliquots that were exposed to atmospheric air for several minutes after the activation procedure. The two resulting isotherms denoted as RWTH-3 and RWTH-4 are plotted in Fig. 7 together with published literature data (see above). The two RWTH isotherms show a very good agreement with those published by Humayun and Tomasko [4] and Sudibandriyo et al. [6] reaching a maximum excess sorption capacity of ~7 mmol/g. The CO_2 excess sorption isotherm for F400 by Pini et al. [5] has a

slightly higher maximum excess sorption capacity (~7.4 mmol/g), ranging between the values of Humayun and Tomasko [4] and Sudibandriyo et al. [6] on the one hand and those of the present study on the other hand. This comparison shows that failure to rigorously adhere to well-defined identical sample treatment procedures can lead to significant discrepancies in CO_2 excess sorption measurements on activated carbons. An alternative, though less likely explanation for such discrepancies could be variability of sorption properties of different batches of activated carbon reflected in slight differences in the results of proximate and ultimate analyses (Table 2).

We acknowledge that the surface area available to CO_2 may be different from that measured by N_2 adsorption. However, the observed differences in N_2 specific surface areas appear to correlate with the differences between our CO_2 sorption isotherms and previously published data [4–6].

The experimental sorption isotherms from the literature and the RWTH-3 and RWTH-4 isotherms were fitted by the three-parameter excess sorption function (Eq. (2)). The parameters resulting from this procedure and information on the quality of the fits are summarized in Table 7.

3.5. Using Helium as reference gas

Both, the gravimetric and the manometric method use helium as reference gas to determine the buoyancy of the sample (gravimetric) or the void volume of the sample cell (manometric). Helium is commonly considered as "non-adsorbing" or the least adsorbing gas. A small degree of helium sorption (which cannot be excluded but also not quantified) will lead to an underestimation of the sample volume for both methods. This, in turn, would result in an error (overestimation) of the excess sorption capacity. As noted by Sakurovs et al. [27], helium adsorption, if present, will be in the μmol g^{-1} range as compared to CO_2 sorption capacity of the F400 sample which is in the mmol g^{-1} range
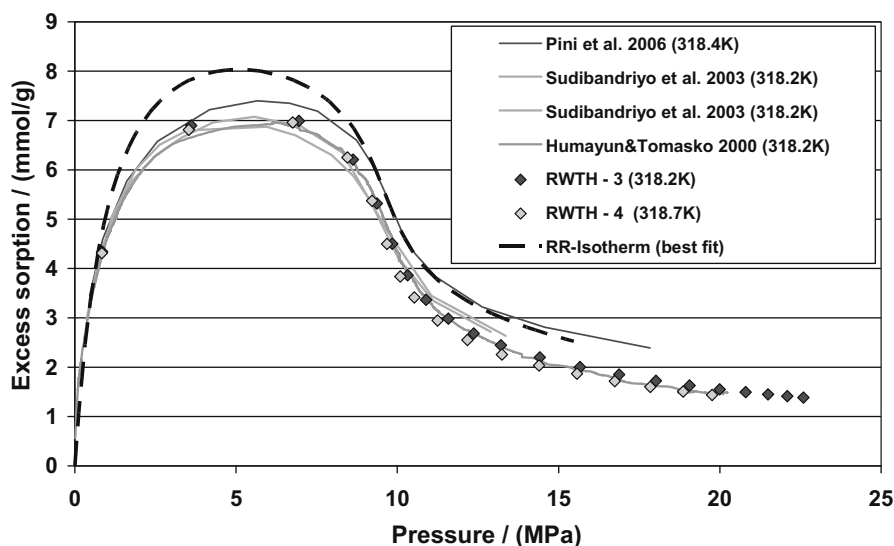

Fig. 7 – Comparison of previously published excess sorption isotherms for CO_2 on F400 activated carbon with two measurements performed at RWTH Aachen on samples exposed briefly to air after activation.

Table 7 – Fit parameters of CO_2 excess sorption isotherms on F400 activated carbon from the literature and RWTH Aachen measurements 3 and 4 (modified drying procedure). Sorbed phase density (ρ_{sorbed}), maximum absolute sorption capacity $s^\infty_{absolute}$ and Langmuir coefficient ($K_{L,V}$) were fitted by regression of Eq. (6).

	Excess sorption at 5 MPa (mmol/g)	T(K)	ρ_{sorbed} (kg/m^3)	$s^\infty_{absolute}$ (mmol/g)	$K_{L,V}$ (MPa)	No. of data points	Quality of fit Δn
RWTH – 3	7.2	318.2	1014	9.5	0.97	21	0.20
RWTH – 4	7.1	318.2	995	9.5	0.98	17	0.17
Pini et al. [5]	7.4	318.4	1043	10.4	1.20	19	0.12
Sudibandriyo et al. [6]	7.0	318.2	1019	9.3	0.94	13	0.12
Sudibandriyo et al. [6]	6.9	318.2	1013	9.2	0.90	13	0.08
Humayun and Tomasko [4]	7.0	318.2	1008	9.5	1.05	4779	

and hence can be neglected. By definition and experimental practice, the manometric as well as the gravimetric sorption experiments represent a differential measuring method with helium as a standard reference gas.

4.   Conclusion

The results of the first phase of the European inter-laboratory test on high-pressure CO_2 sorption show an excellent agreement of the results obtained by the four participating laboratories. The deviations of the sorption isotherms are less than 5% and the intra-laboratory reproducibility is better than 1% for each laboratory. One result of the study is the excellent agreement of isotherms obtained from different methods, i.e. manometric and gravimetric, for well-defined and controlled sample preparation and starting conditions.

Excess sorption values measured in this study are consistently higher than those reported in the literature for the same sorbent/sorptive system (F400/CO_2). This offset is most likely due to differences in the initial conditions (activation and drying of the samples) but could also reflect variability in the batches of F400 used (Table 6).

A three-parameter excess sorption function based on a Langmuir-type absolute sorption function was found to be adequate to represent the experimental data of this study with sufficient accuracy within the limits of present-day experimental uncertainties. The "EU-Round Robin" parameter set reported in Table 5 is considered to define the presently highest quality excess sorption isotherm for CO_2 on F400 at 318 K.

The determination of accurate high-pressure sorption isotherms for CO_2 still represents a challenge. However, the increasing number of published high-quality data indicates that significant progress has been made during recent years.

Inter-laboratory studies can help to identify and avoid pitfalls and to formulate standard procedures that improve overall data quality. The present study has revealed a number of potential experimental problems in particular of the manometric procedure and has identified strategies to avoid or minimize their impact on data quality. Thus, apart from using high performance pressure and temperature sensors, careful adjustment of pressure steps during the measuring procedure is recommended. Finally, the importance of well-defined procedures for sample preparation is emphasized.

The results presented here provide a benchmark for future studies on the sorption of supercritical CO_2 on natural coals

and help to improve and optimize the experimental standards. Meanwhile, several other laboratories world-wide have joined this initiative and have been supplied with samples and instructions. Work is presently in progress to determine high-pressure excess sorption isotherms of CO_2 on selected natural coals with the same level of accuracy as for the F400 activated carbon.

Appendix A.   Supplementary data

Supplementary data related to this article can be found, in the online version, at doi:10.1016/j.carbon.2009.06.046.

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