Factors Influecing the Amount of CO_2 Sorbed on Coal

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ABSTRACT: This paper deals with factors influencing sorption of carbon dioxide on coal which understanding is necessary for detailed study of in situ processes. The effect of temperature, pressure, moisture, and grain size on the sorption affinity for CO_2 at sub- and supercritical temperatures within the range of 15-70 °C and subcritical pressure below 8 bar has been studied on dry and moist (0.6 and 1.1 % water, respectively) samples of bituminous coal from the Darkov mine (Czech part of the Upper Silesian Basin). Physical adsorption has been identified as a predominant sorption process. Sorption measurements were carried out, observing the effect of temperature in both isothermal and isobaric mode which provided comparable results. The adverse effect of temperature is attenuated by increasing pressure which can be considered as a dominant factor of the sorption process. A marked decrease in the sorption capacity is recorded already by quite low water content; the sorption capacity of a dry sample at 25 °C decreases by up to 67 % in a sample with 1.1 % moisture at 45 °C. Longer period to reach the sorption equilibrium observed on coarse grained coal indicates that CO_2 sorption in a coal seam is a process which fill longer time interval.

KEY WORDS: sorption of CO_2, carbon dioxide, coal sorption capacity, temperature and pressure, moisture content, grain size.

Introduction

Regarding carbon dioxide as an important greenhouse gas, the ways of reduction of its emissions are of great interest. One of the ways of the reduction is capturing CO_2 emitted into the atmosphere and its long-term storage within suitable disposal sites including coal strata. Investigation of CO_2 sorption at laboratory scale has been of a primary interest as a support of the developing technology ECBMR (Enhanced Coal Bed Methane Recovery) which resolves storage of CO_2 together with the increase in the effectiveness of CBM exploitation (van Bergen et al. 2004).

Selection of a site with high storage capacity for CO_2 requires knowledge of coal textural properties, which control the mechanism and extent of the storage, as well as the strength of bonding of the sorbed gas. The efficiency of the interaction process depends on the molecular properties of CO_2 and physico-chemical nature of the external centres of coal matter.

Sorption processes (sorption in micropores and on the surface of meso- and macropores, absorption) taking place in the coal porous system can be considered as the main storage mechanisms. They depend particularly on the pressure and temperature conditions in situ, where CO_2 can be present in coal both at sub- and supercritical temperatures ($T_c = 33.1$ °C) as well as at sub- and supercritical pressures ($P_c = 7.4$ MPa), and on the presence of seam water. Kinetics of the sorption process in situ is affected by compactness of coal matter. The combined effects of sub- and supercritical temperatures and subcritical pressures on dry and moist samples of coal with various grain sizes were studied in laboratory conditions. The effect of these factors on the sorption process has been evaluated.

Experimental

Sample description

The study was carried out on the Darkov bituminous coal from the Czech part of the Upper Silesian Basin. Its basic characteristics are given in the Table 1.

Table 2. presents textural parameters of coal. Determination of the volume of meso- and macropores V_{mm} and their surface area S_{mm} were carried out by high-pressure porosimetry (Maha-

Sample	Depth [m]	C^{daf} [wt. %]	H^{daf} [wt. %]	V^{daf} [wt. %]	R_o [%]	V [vol. %]	L [vol. %]	I [vol. %]	MM [vol. %]
Darkov	95.6	87.11	5.03	28.36	1.14	55.8	8.5	31.4	4.3

C^{daf} – carbon content (dry ash free basis), H^{daf} – hydrogen content (dry ash free basis), V^{daf} – volatile matter (dry ash free basis), R_o – reflectance, V – vitrinite, L – liptinite, I – inertinite, MM – mineral matter

■ **Tab. 1.** Basic chemical and petrographical characteristics of the bituminous coal by experiments.

Sample	d_r [g/cm^3]	V_{micro} [cm^3/g]	S_{micro} [m^2/g]	r_{mode} [nm]	V_{mm} [cm^3/g]	S_{mm} [m^2/g]	r_{avr} [nm]
Darkov	1.4136	0.03747	102	0.67	30.9	4.2	4.9

d_r – real density, V_{micro} – volume of micropores, r_{mode} – modus of micropores radii, S_{micro} – surface of micropores, V_{mm} – volume of meso- and macropores, S_{mm} – surface of meso- and macropores, r_{avr} – average pore radius of meso- and macropores

■ **Tab. 2.** Textural characteristic of coal sample.

jan and Walker 1978) on an apparatus Pascal 240 by Thermo Electron-Porotec in the pressure range 0.1 to 200 MPa corresponding to the radii interval 3.7 to 7,500 nm. Measurements were carried out on particles with size of 5 mm. Calculation of the volume V_{micro} and surface area S_{micro} of micropores were performed from the CO_2 isotherm which was meassured at 25 °C and evaluated according to Dubinin's theory of volume filling. Dubinin's and Medek's equations (Dubinin 1960, Medek 1977) were applied.

Gravimetric sorption analysis

Sorption measurements were carried out using an Intelligent Gravimetric Analyser (IGA002) by Hiden Analytical. This instrumental system (Benham and Ross 1989) measures weight of a sample as function of time with gas pressure and sample temperature, and thus enables determination of the sorption isotherm simultaneously with kinetics of the adsorption and desorption processes at individual pressure points. The IGA system works with a thermostated bath within the temperature range of 5 to 80 °C up to the maximum pressure of 10 bar, and introduces automatically a correction for buoyancy.

Approximately 100 mg of sample was used for each measurement. Initially the sample was outgassed at 105 °C until a constant weight was achieved at 10^{-6} Pa. Sorption of CO_2 was realized in both isothermal and isobaric mode on fine grains (<0.2 mm) and coarse particles (>5 mm). Isotherms were measured at the temperatures 15, 25, 35, 45, 55 and 65 °C, and the final pressures 1 and 8 bar. Isobars were measured at the pressures 200, 500, 1,000 and 2,000 mbar in a temperature sequence from 15 to 70 °C when desorption was the controlling mechanism. The measurements on moist samples were realized by two-stage sorption of water vapour and CO_2. The sorption of water vapour was carried out up to the relative pressures of 0.19 and 0.46 corresponding to the moistures of 0.6 and 1.1 %, respectively. The moist sample was then exposed to subsequent CO_2 sorption.

In the course of the sorption process, sample temperature was automatically controlled within the range of ± 0.05 °C, the pressure converter used worked with accuracy ± 0.02 %. The long-term stability of the microbalance was ± 1 µg with a weighing resolution of 0.2 µg. Approaching the equilibrium state was analyzed in time and the weight change was recorded upon reaching 98 % of an asymptotic value according to a computer algorithm.

Results and discussion

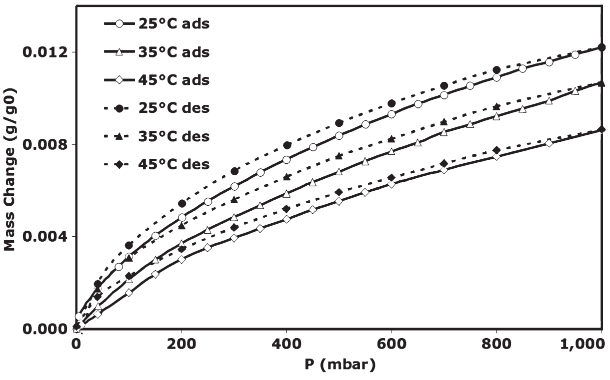
Coal as sorbent

Among natural porous substances, an exclusive position is occupied by coal, which was formed by long term action of temperature and pressure by anaerobic chemical transformation of plant tissues resulting in coalification of original plant matter. Coal has typical properties of a gel, number of gases and vapours easily dissolve in it hand in hand with its swelling, and moreover it readily reacts with selected gases producing chemisorption complexes. Within its inner three-dimensional arrangement, coal preserved a substantial part of the porous structure of original plant material with predominance of cavities with the effective size <2 nm. Generally, coal can be classed among the substances with the three-dispersed porous structure for which the research of the arrangement of the porous texture resulted in the common knowledge of the microporous character of the solid phase.

Similarly to other polymeric substances, particularly of gel character, coal allows two-component sorption of CO_2 as a combined process (Larsen 2004), which consists generally of a fast process of physical adsorption with equilibration time of the order of seconds to minutes, and a slow process connected with formation of dissolution of gas in solid phase, connected with reinforced binding of molecules with the solid phase (McBain 1932). As a process complementary to absorption, chemisorption has also to be considered which can show on the isotherm similarly as absorption. Chemisorption can be usually excluded or confirmed with respect to probability of a chemical reaction of adsorbate with adsorbent. These sorption processes take place simultaneously and are inseparable. The presence of a slow process, e.g. absorption or chemisorption, can be shown in the form of the desorption branch of the isotherm situated more or less over the adsorption branch (Medek et al. 2006).

The total quantity which can be present in coal bed is possible to divide into five basic forms of bond: the part adsorbed in micropores, second one absorbed in macromolecular matter, third - adsorbed on the surface of meso- and macropores, fourth – freely mobile in the pore space unfilled by water and finally, in case of water incursion, the last one dissolved in the present pore water. Dominant part of CO_2 is bound in micropores and according to coal type the part dissolved in macromolecular structure of coal (Weishauptová and Medek 1998, Mastalerz et al. 2004).

Table 2 presents textural parameters of studied coal, from which it is obvious that the prevailing part of the porous system is formed by micropores cavities, which are a prerequisite of its sorption ability. From the CO_2 isotherms depicted in the Fig.1, the general reversibility of the sorption and desorption branches is obvious, when almost all the CO_2 is desorbed at a near to zero pressure. If the residual non-desorbed amount of CO_2 is considered absorbed, then it represents only 4.5 % and 1.3 % of the to-



■ **Fig. 1.** Adsorption / desorption CO_2 isotherms at 25, 35 and 45 °C up to 1,000 mbar on fine grains.

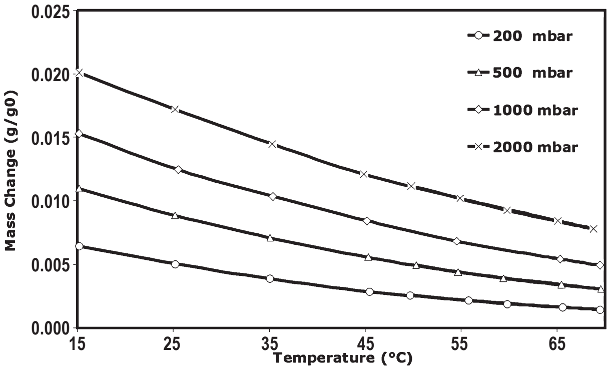
tal amount sorbed at 25 °C and 45 °C, respectively. From this it can be assumed that in the case of the Darkov coal, the physical adsorption is the predominant sorption process under given experimental conditions.

Dependence of CO_2 sorption by coal on temperature

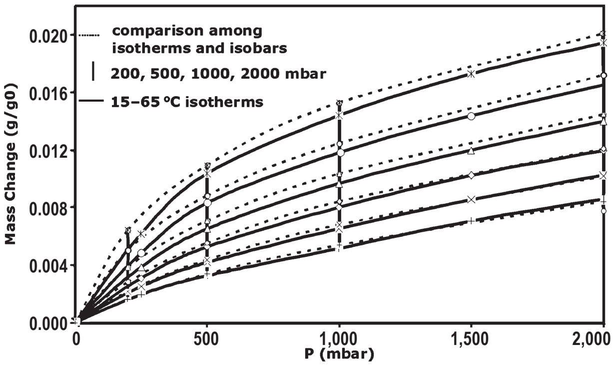
It is generally accepted that the sorption capacity of coal markedly decreases with increasing temperature (e.g., Kroos et al 2002). Like the adsorption, also absorption is affected by temperature; absorption decreases with increasing temperature much more rapidly than adsorption for molecules of a size comparable with CO_2 (White et al. 2005). The isotherms measured for Darkov coal at the subcritical temperature 25 °C and supercritical temperatures 35 and 45 °C at the subcritical pressure 1000 mbar show about 30 % increase of mass reduction between 25 and 45 °C (Fig. 1). This effect has been caused by changes in the porous system in the dependence on increasing temperature, when constriction of maximum pore diameters occurs, as well as by the properties and behaviour of CO_2 under subcritical and supercritical temperatures, when kinetic energy of the gas molecules increases at supercritical temperatures. This limits number of pores, which can be completely filled. The real micropore volume in coal is always higher than that assessed on the basis of sorption capacity measurement, e.g., at 35 or 45 °C, and hence, determination of the total micropore volume is carried out at a subcritical temperature (Sakurovs et al. 2008) .

Fig. 2 documents the increase of mass reduction due to increasing temperature, which has been measured in the isobaric mode instead of the common isothermal mode. The isobars corresponding to a polynomic dependence are an advantage for determination of the sorption capacity for a given pressure within the measured range of temperatures.

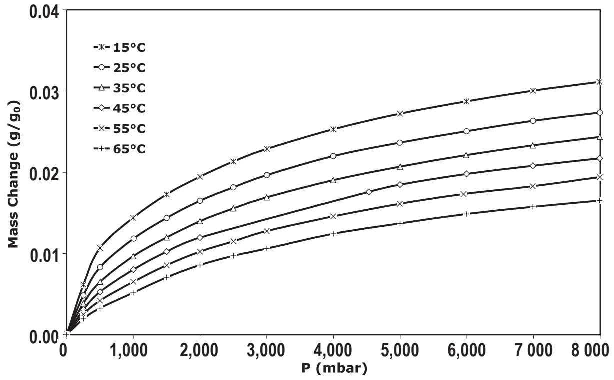
Comparing the sorbed amounts derived from isotherms and isobars (Fig. 3) it has been found that at the temperatures 15, 25, and 35 °C, CO_2 isobars provided a higher mass uptake compared with isotherms at the same conditions. The difference at 25 °C and 1 bar was less than 2 % of the mass uptake, which can be attributed to a scatter of results of repeated isotherm measurement. At higher temperatures 45, 55, and 65 °C, equal mass uptake were obtained in the isothermal and isobaric modes. It can be assumed that at lower temperatures, due to the desorption character of measurement, the sorption heat is partially carried off from the sample surface, whereby also the sorption equilibrium is achieved more quickly, which can be reflected in a higher value of the mass uptake.



■ **Fig. 2.** CO_2 isobars at 200, 500, 1,000 and 2,000 mbar within the temperature range from 15 to 70 °C on fine grains.



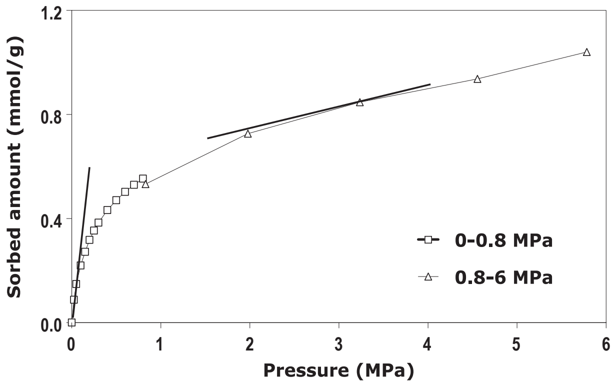
■ **Fig. 3.** CO_2 isotherms within temperature range from 15 to 65 °C and final pressure 2,000 mbar together with isobars for 200, 500, 1,000 and 2,000 mbar and temperatures from 15 to 65 °C.



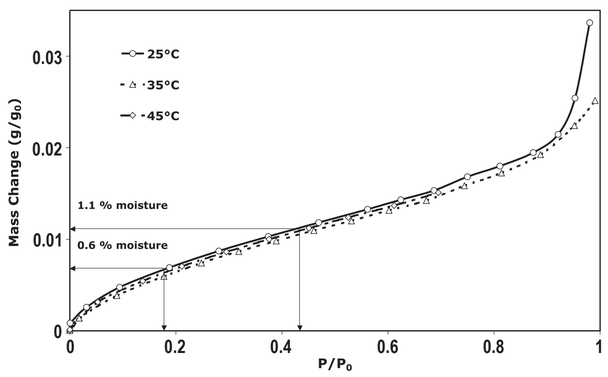
■ **Fig. 4.** CO_2 isotherms from 15, 25 to 65 °C up to pressure 8,000 mbar on fine grains.

Dependence of CO_2 sorption by coal on pressure

In the case CO_2, sorption until pressures < 6 MPa is generally considered as the low-pressure sorption corresponding to the Langmuir model (Langmuir 1916, Krooss et al. 2002, Goodman et al. 2007), whereas the high-pressure sorption > 6 MPa shows according to many authors abnormal behavior (Goodman et al. 2007, White et al. 2005). Fig. 4 shows the CO_2 isotherms for the temperature range 15–65 °C measured up to the pressure of 0.8 MPa. Although the sorbed amount decreases with increasing temperature, increasing pressure significantly increases this amount. An increase in temperature from 15 to 65 °C at 1 bar pressure causes almost 3 times lower CO_2 sorption, whereas at 8 bar pressure the sorption is only 2 times lower. The ratio of the amounts sorbed at 8 and 1 bar increases linearly with temperature. This is an evidence that pressure is a dominant factor affecting CO_2 sorption. Within an interlaboratory cooperation with Institute of Geology and Geochemistry of Petroleum



■ **Fig. 5.** CO_2 isotherm at 35 °C up to pressure 6 MPa.



■ **Fig. 6.** Water vapor isotherms at 25, 35 and 45 °C on fine grains.

and Coal, RWTH Aachen University, sorption has been measured up to 6 MPa at 35 °C. Despite a different method applied (volumetric sorption), the amounts adsorbed at 0.8 MPa is well comparable (Fig. 5). The amount sorbed at 6 MPa was roughly twice more that sorbed at 0.6 MPa. The highest increase occurs, as evident from the isotherms in Fig. 5, at low pressures below about 0.1 MPa, but from the pressure 3.2 MPa the mass uptake decreases asymptotically.

Dependence of CO_2 sorption by coal on moisture content

For a more accurate simulation of the in situ conditions, the sorption isotherm is measured mostly on both dry and moist coal (e.g. Kroos et al. 2002). At the assessment of CO_2 interaction with the system water/coal, water sorption on coal can be considered as primary mechanism. With respect to their polar character, water molecules are attracted by the active centers on the coal surface, followed by forming clusters of the associated water molecules around these centers via hydrogen bonds. At a sufficiently high pressure the clusters associate forming a condensed monomolecular layer and further increase of the relative pressure induces multimolecular adsorption, or even capillary condensation. Adsorption isotherm of water is a function of concentration and distribution of the active centers, porous structure, and water vapour pressure. The character and concentration of the active centers determine the hydrophilic degree of coal. From the shape of water vapour isotherms in the Fig. 6, where a steep slope is not observed until the relative pressure of 0.5, it is evident that at the moistures of 0.6 and 1.1 % chosen for the subsequent CO_2 sorption the multimolecular adsorption and/or capillary condensation did not occur.

Contrary to water molecules, the specific centers in the surface are not necessary for CO_2 sorption, and also a different interaction of this adsorbate with the coal surface can be expected (White et al. 2005). The presumption that the sorption of CO_2 on coal is realized by the process of volume filling simplifies evaluation of the interaction of CO_2 with moist coal (Sakurovs et al. 2008). In the mechanism of volume filling, where the augmented adsorption potential of opposite micropore walls takes effect, CO_2 moves relatively freely along the surface and the adsorbed water can hinder the access to the microporous system. The active centres occupied by water molecules together with the limited access to micropores create the complex character of the sorption on moist coal, which is always lower than on dry coal.

Fig. 7 illustrates a comparison of CO_2 sorption on dry coal and the coal with 1.1 % moisture, Table 3 presents the respective reduction in the adsorption capacity.

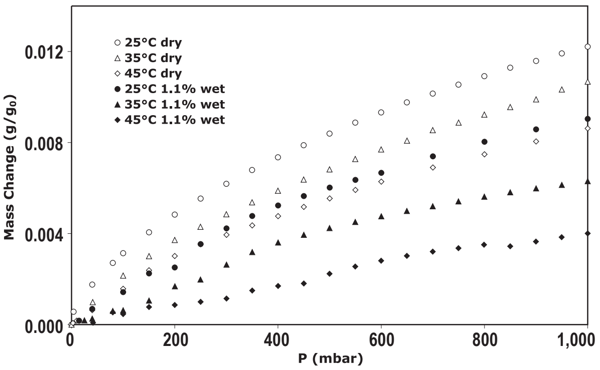
Reduction in the sorption capacity increases linearly with increasing water content and temperature. The joint effect of temperature and moisture has been reflected in a 67 % decrease in the adsorption capacity of a coal sample with 1.1 % moisture at 45 °C compared to a dry coal sample at 25 °C. From this it has followed that the real amount of CO_2 sorbed in situ strongly depends besides temperature and pressure also on coal moisture.

Dependence of CO_2 sorption by coal on size of grained coal

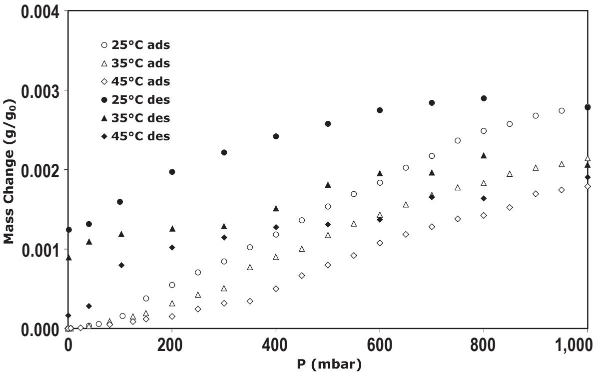
Most of sorption studies following the effect of several variables have been carried out with very finely grained coal samples (e.g., Mastalerz et al. 2004). These studies, however, do not consider the integrity of coal matter in situ, which significantly affects the CO_2 sorption kinetics (Busch et al. 2004). A comparative study of CO_2 sorption on fine grains and coarse particles at the temperatures 25, 35 and 45 °C and pressure 1 bar has been conducted. The coarse particle size was chosen about 25 times higher that that of the fine grain and the time dependence

Temperature [°C]	Mass uptake [mg/g]		Sorption capacity reduction at 0.6 % [%]	Mass uptake [mg/g] 1.1 % moist	Sorption capacity reduction at 1.1 % [%]
	Dry coal	0.6 % moist			
25	12.216	10.081	17.5	9.042	26.0
35	10.677	7.979	25.3	6.302	41.0
45	8.618	5.838	32.3	4.005	53.5

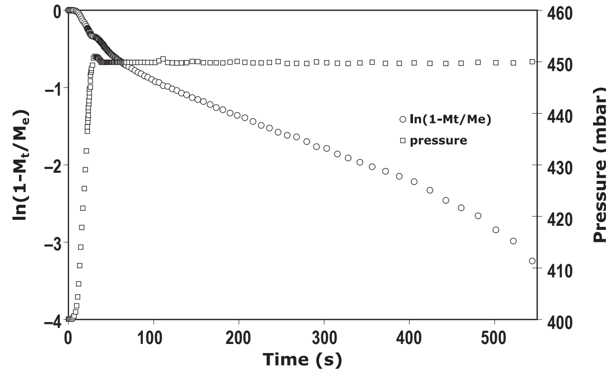
■ **Tab. 3.** Comparison of the effect of 0.6 and 1.1 % moisture content on the sorption capacity of fine grained Darkov coal.



■ **Fig. 7.** Comparison of CO_2 sorption on dry sample and coal sample with 1.1 % moisture content in fine grains.



■ **Fig. 8.** Adsorption/ desorption CO_2 isotherms at 25, 35 and 45 °C up to 1,000 mbar on coarse particles.



■ **Fig. 9.** Example of CO_2 adsorption kinetics (25 °C, pressure range 400–450 mbar, fine grain).

of mass uptake equilibration during individual pressure steps of sorption experiments was monitored. The isotherms in Fig. 8 show that the various grain sizes has not been reflected in the isotherm shapes, which in both cases obey a comparable temperature trend. However, in the case of coarse grain the adsorption and desorption branches are not reversible. Expectedly, approach to the sorption equilibrium is considerably slower in the coarse grained coal than in the fine grained coal. Thus also the contact between CO_2 and coal matter is prolonged, thereby the probability of gas absorption within the coal matrix is increasing. Disturbance of the sorption reversibility can be caused by both, the absorption and a reduced desorption ability of the bulk matter.

Sorption kinetic was determined from the mass uptake equilibration in time. The rate constants were calculated according to modified empirical diffusion equation $M_t/M_e = 1 - e^{-kt}$ (O'koye et al. 1997) where M_t equals gas uptake at time t, M_e equals gas uptake at equilibrium, t is time and k is rate constant. The rate constant represents the slope of the rectified dependence $\ln(1-M_t/M_e)$ against time (Fig. 9).

The comparison of the rate constants for different grain sizes at a constant pressure and the temperatures 25, 35, and 45 °C is given in the Table 4. It is obvious that at the same pressure range and given temperature the rate constants significantly decrease with increasing grain size. The effect of temperature on the rate constant especially for fine grains is shown to be very small.

Conclusions

In this study an experimental information has been collected which allows to conclude:

- Although the sorbed amount decreases with increasing temperature, it is significantly enhanced by increasing pressure.
- Only a small amount of moisture content in coal may reduce the adsorption capacity very markedly
- Equilibration time increases and adsorption rate decreases, with increasing grain size for all experimental conditions. The slower approach to the sorption equilibrium on coarse grained coal can cause a longer time interval at the CO2 storage in situ.

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Pressure range	Temperature	Fine grains	Coarse particles	Fine grains	Coarse particles
[mbar]	[°C]	Mass uptake [mg.g^{-1}]		Adsorption rate constant [x 10^{-4}.s^{-1}]	
400–450	25	4.167	0.361	6.26	0.98
	35	3.491	0.285	6.10	0.31
	45	0.409	0.291	5.08	0.26

■ **Tab. 4.** Comparison of the CO_2 sorption rate constants for fine grains and coarse particles over the pressure range 400–450 mbar at 25, 35 and 45 °C.

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